# Malathion Reregistration Eligibility Document Environmental Fate and Effects Chapter

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# Introduction

# Limitations and Agreements With Registrants Regarding the Uses and Application Scenarios Reviewed and Supported

Registrants who presently intend to support reregistration of malathion products have been contacted and informed that only those use rates presently supported by food tolerances will be reviewed for this Reregistration Eligibility Document. Those crops where tolerances do not exist or where no support from registrants has been received by the Agency are considered revoked and will not be addressed in EFED's risk assessments for Malathion reregistration. Non-food uses of Malathion will be reviewed as has been done with previous REDs. High exposure scenario risk presumptions will be based on the maximum labeled rates, maximum permitted seasonal applications and minimum recommended intervals for these use patterns. The Cheminova and IR-4 Malathion teams have presented proposed uses and application scenarios they intend to support.— Any labels which exceed the rates or permitted maximum seasonal applications, or that specify minimum application intervals which are less than the rates presented by these groups will require additional environmental assessment and review.

#### Temporal Uncertainties of Tolerance Test Scenario Use In Risk Assessments

Assumptions of lower use rates, longer intervals, and limited numbers of seasonal applications based on maximum tolerance tested rates may lead to prediction of lower risk potential than what will occur while mandatory label revisions are in progress. Some malathion labels presently permit application rates well in exceedance of maximum tolerance rates of 6.25 lb ai/A(8.0 to 25.0 lbs ai/acre presently listed on several product labels). The time limits for revision of existing labels will impact the currency of the present assessment for malathion impacts on wildlife and aquatic organisms. This may be tempered by the fact that higher rates, shorter intervals, and unlimited seasonal applications are not as economically practical for the user community and for that reason not common practice. However, given the number of uses and products containing malathion and the number of registrants producing these products, it is expected that application restrictions and mitigation measures may not be implemented for several years pending final agreements with registrants.

# **Use Characterization**

## **Historical Perspective**

Malathion has been used for 45 years and is manufactured in over 50 locations throughout the world. Though malathion has been manufactured by a variety of companies, the technical formulation portion of the U.S. business was purchased by Cheminova Agro from American Cyanamid in 1991. As of 1994, all technical malathion used in the U.S. is marketed and distributed by Cheminova.

## Summary of Supported Product Types, Formulations, and Use Scenarios

Product Numbers, Types and Percent Active Ingredient

Technical malathion is produced by Cheminova Agro for the U.S. market. At this time 63 formulators of pesticide products use malathion as an active ingredient. Approximately 235 malathion products are produced by these 63 formulators. Some of these products also contain active ingredients other than malathion (e.g., methoxychlor).

Product types include technical ingredient for formulation use, emulsifiable concentrates, wettable powders, dusts, and ready to use (RTU) formulations. There are no granular malathion products presently registered, although malathion is used in a variety of bait type formulations or mixed and applied to food baits for attraction of target insects.

The percent of malathion employed in these 235 products varies considerably and ranges from less than 3% for many of the homeowner use RTU's to as high as 96% malathion for ULV formulations.

#### **Use Scenarios**

The majority of agricultural and public health uses involve the mixture or dilution of EC formulations with water for aerial or ground spray application to target areas either as ULV applications, standard ground application sprays, or ground fogs. Wettable powders are generally diluted in 1 to 100 gallons of water and applied to plant surfaces by ground spray methods. Dust formulations are often used for treatment of grain storage areas or the actual grain itself. Ready to use formulations are often used in the home and applied directly to the insect pest or to areas where the pest is observed. Uses of malathion for direct application to livestock is not being supported. Forest uses on public lands are not being supported, though use on tree farms is still permitted.

## Summary of Major Uses Nationwide

Cheminova has divided the malathion market into four major portions; USDA special program use, commercial agriculture, public health use, and home and garden use. Actual tonnage use estimates are considered confidential business information, the percentages of use can be broadly summarized as USDA, 59-61%; General Agriculture, 16-20%; Public Health, 8-15%; and home and garden use, 10%. These percentages of use may vary with fluctuations in pest pressure or concerns for public health which might occur following natural disasters, e.g. a hurricane.

## Summary of USDA Special Program Uses

The Boll weevil Eradication Program for cotton crops in the lower states account for the greatest proportion of use by USDA as well as the nation as a whole. Over 97% of USDA's uses of malathion have been towards efforts to eradicate the Mexican boll weevil from U.S. cotton crops. In 1997 USDA applied over 10 million pounds of malathion active ingredient primarily by aerial ULV methods to areas of infestation in Texas and Alabama. Large portions of Texas, Louisiana, Mississippi, and Alabama are targeted for 1998. States where heavy infestations have been eradicated, but lower preventative uses are sometimes still employed, include California, Arizona, Georgia, South Carolina, North Carolina, and Virginia. In general, 10-12 oz. of product (about 1.0 lb of active ingredient) are aerially applied 6-8 times per acre before, during and after the cropping season.

Other programs comprising about 2% of USDA malathion use include the Mediterranean Fruit Fly Control Programs in Florida and California and Grasshopper Control on Federal Rangelands in the western states. Nationwide USDA use has ranged from 80,000 to 360,000 lbs of ai for these programs depending on pest sightings or pressure. Medfly applications generally involve mixture of malathion into a hydrolysate bait at about a 20% malathion concentration which is then applied two to four times at 0.175 lb ai/acre by aircraft or ground spray equipment.

## Summary of Public Health Uses

Mosquito control in populated and rural areas comprises the major use of malathion for public health uses. In general, public health use would be necessitated by actual or potential disease outbreak caused by a particular pest. A recent example was the 1999 West Nile Virus spraying program implemented by New York. Though mosquito control does potentially prevent such outbreaks (particularly after hurricanes or major storms) much of the application is also performed when a disease problem has not been documented. In some areas, numerous public complaints to local mosquito control officials may be adequate incentive to implement spraying operations. This type of use is particularly heavy near coastal resort areas, where high bite rates constitute a potential loss of tourist revenue and therefore an incentive for active spraying programs. High use of adulticides is generally an indication that larvicidal uses of pesticides during the early breeding season have failed to control population outbreaks.

## Summary of Supported Agricultural Crop Uses

Approximately 100 food crop uses of malathion are being supported by Cheminova and IR-4. In the past many labels have often **not** reflected the application rates, intervals, and maximum numbers of application on which acceptable tolerance levels were based. Many of the over 250 product labels were written with no specified intervals or limitations on the numbers of applications which could be made to crops. In an effort to standardize the acceptable label rates for reregistration purposes, Cheminova and IR-4 have agreed to specify maximum rates, minimum intervals, and maximum seasonal application numbers that they support for food uses (see table which follows). Crop scenario codes are indicated by letters for each separate application rate (lbs ai/A), followed by numbers for maximum proposed multiple applications, and (number of days) for the intervals proposed between applications. Thus A10 (7D) indicates an application of 0.175 lbs ai/A is permitted 10 times during the growing season with a minimum interval between applications of 7 days. Many crops may fall under the same application scenario or in some cases only one crop is proposed for that particular scenario. These scenarios are later used in EEC and Risk Quotient tables and allow the reader to associate each value with a particular crop or use

pattern.

Table 1.

# Malathion Use Rate Table - Crop Scenarios Cheminova and IR4 Supported Maximum Tolerance Rates

						Numb	er of App	lications					
	lb ai/ A	Int. Day	1	2	3	4	5	6	7	8	9	10	12 - 25
A	0.17	7D	A1									A10(7D)	
В	0.50	NA	B1										
В	0.61	5D	C1				C5(5D)						
C	0.61	7D		C2(7D)	C3(7D)								
C	0.61	14D		C2(14D)									
D	0.76	10D	D1				D5(10)						
E	0.94	3D	E1			E4(3D)							
E	0.94	6D						E6(6D)					
E	0.94	7D			E3(7D)								
F	1.0	7D	F1					F6(7D)					
G	1.25	3D	G1	G2(3D)				G6(3D)					G 25
G	1.25	5D					G5(5D)						
G	1.25	7D		G2(7D)	G3(7D)	G4(7D)	G5(7D)	G6(7D)	G7(7D)	G8(7D)	G9(7D)	G10(7D)	
G	1.25	14D		G2(14D)									
Н	1.50	7D			H3(7D)		H5(7D)						
I	1.56	7D		I2(7D)				I6(7D)					
J	1.88	5D					J5(5D)						
J	1.88	7D			J3(7D)	J4(7D)		J6(7D)					
J	1.88	14D		J2(14D)									Щ
K	2.03	6D						K6(6D)					
K	2.03	7D			K3(7D)	K4(7D)							
L	2.5	3D											L 25
L	2.5	5D			L3(5D)								
L	2.5	7D			L3(7D)		L5(7D)						
M	3.43	5D					M5(5D)						
N	3.75	7D				N4(7D)		N6(7D)					
N	3.75	14D				N4(14D)							

	Rate lb ai/A	Int. Day	1	2	3	4	5	6	7	8	9	10	12- 25
o	4.7	30D		O2(30D									
P	5.0	7D			P3(7D)	P4(7D)							
Q	6.25	30D		-	Q3(30D								

A10=Orange, Grapefruit, Lemon, Lime, Tangerine, Tangelo, and Kumquat 0.175 lb ai/A 0.50 lb ai/A **B1**=Flax 0.61 lb ai/A C5(5D)=Sweet Corn, C2(7D)=Hops, C3(7D)=Beans, Corn, Rice, Sorghum, Wheat, and Rye C2(14D)=Alfalfa, Clover, Lespedeza, Lupine and Vetch 0.76 lb ai/A **D5**=Blueberry 0.94 lb ai/A E1(3D)=Grass for hay, E4(3D)=Mushroom, E6(6D)=Strawberry, E3(7D) = Peppermint and spearmint, E7(7D)=Macadamia 1.0 lb ai/A **F6(7D)**=Melons, Watermelon, Pumpkin and Winter Squash 1.25 lb ai/A G1(3D)=Grass for hay, G2(3D)=Field corn, G2(7D) Brussel sprouts, cauliflower, collards, kale, kohlrabi G6(3D)=Mustards, G25(3D)=Cotton, G5(5D)=Watercress, G3(7D)=Rice, Sorghum, Wheat, Rye, Barley, Oats and Corn, G4(7D)=Blueberry (ULV), G5(7D)=Turnip, Broccoli, Apple, Sweet Corn, Beet, Horseradish, Parsnip, Radish, Rutabaga, Salsify, G6(7D)= Cabbage and Cherry(ULV), G7(7D)=Carrot, G8(7D)=Mango and Passion fruit, G9(7D)=Asparagus G10(7D)=Pears and Quince, G12(7D)=Guava and Papaya, G2(14D)=Alfalfa, Clover, Lupine, Vetch and Lespedeza **H2(7D)**=Celery, **H6(7D)**=Okra 1.5 lbs ai/A 1.56lbs ai/A I2(7D)=Potato, Sweet potato, I5(7D)=Onion, Garlic, Shallot, Leeks J6(5D)=Lettuce, J4(7D)=Blackberry, Raspberry, Loganberry, Boysenberry, Dewberry, Currant, 1.88 lb ai/A Gooseberry, J3(7D)=Cucumber, Chayote, J6(7D)= Strawberry, J2(14D)=Grapes K6(6D)=Strawberry (50% WP), K3(7D)= Spinach, Dandelion, Endive, Parsley and Swiss Chard, 2.03 lbs ai/A K4(7D)=Blackberry, Raspberry, Gooseberry, Loganberry, Dewberry, Currant and Boysenberry L25(3D)=Cotton, L3(5D)=Figs, L3(7D)=Mustards, Walnuts, and Pecans, L5(7D)=Peas 2.50 lb ai/A 3.43 lb ai/A M5(5D)=Tomato, Pepper, Eggplant N4(7D)=Apricots, N6(7D)=Cherry, 3.75 lb ai/A N4(14D)=Peach and Nectarine 4.7 lb ai/A O2(30D)=Avocado 5.0 lb ai/A **P3**(7**D**)=Pineapple, **P4**(7**D**)=Chestnuts 6.25 lb ai/A Q3(30D)=Oranges, Grapefruit, Lemon, Lime, Tangerine and Tangelo

#### **Commercial Non Food Crops**

Malathion is presently supported for registration on several non-food crops. These crops include ornamental flowering plants, ornamental lawns and turf, nursery stock plants, ornamental woody plants, pine seed orchards, Christmas trees(commercial), and slash pine.

Previous non-food crop uses which are not being supported by Cheminova or IR-4 include forest uses on douglas fir and spruce(for spruce budworm), hemlock(for hemlock looper), pine trees(for European pine sawfly & Saratoga spittlebug) and larch(for larch casebearer). No registrant has indicated support for reregistration of malathion for tobacco and therefore it is assumed this use will be revoked.

### **Non-Crop Uses-Agriculture Related**

<u>Storage of Grains</u>: Malathion 6% dust formulation is being supported for treatment of stored corn, wheat, barley, oats and rye.

<u>Livestock Feed Lots and Holding Pens</u>: Though direct applications to livestock are no longer supported, treatments of holding facilities and feed lots are still being supported. These treatments are primarily for control of flies and mosquitoes and may be used as sprays or in bait formulations.

<u>Beet Leafhopper Control-Non-Agricultural Lands:</u> This program is confined to specific target areas on non-agricultural lands to control the spread of this pest. The use appears on the Fyfanon ULV and 8EC labels (page 2).

<u>Grasshopper Control Non-Federal Lands</u>: These programs are carried out to control aphids, grasshoppers, and leafhoppers in pasture and rangeland. The Fyfanon 8EC label specifies a mixture of malathion with diesel fuel.

<u>Fly Control-Cull Fruit and Vegetable Dumps</u>: Fyfanon labels contain this use to control drosphilia flies and dried fruit beetles around vegetable and fruit dumps. The 8EC label specifies application as a concentrated drench.

## **Summary of Other Non-agricultural Uses**

#### **Commercial Use Urban Scenarios**

<u>Homeowner Use</u>: Malathion is formulated into numerous home and garden sprays for non commercial use on vegetables, fruit trees, ornamental plants and flowering shrubs, turf, and outside structures. Many are ready to use sprays or dusts and many are combined with other active ingredients.

## Use Around Commercial Buildings and Warehouses

Malathion is used to treat for a number of nuisance pests around warehouses, storage yards, inside buildings, outside perimeters of commercial buildings, etc

Table 2.

MALATHION NON AGRICULTURAL USE SUMMARY

MALATHION NON AG	TO CET	THIL COL		
USE LOCATION WHERE RATE APPLIES (MAX RATE in lbs ai/A)	Max. Rate	Max # Applic.	Min. Interv.	Predicted U.S. Acreage (EPA/OPP)
Nonagricultural rights of way/fencerows/hedgerows	0.598	NS	NS	17,000
Mosquito Control  Lakes/Ponds/Reservoirs(human use)(0.5985)  Nonag. Uncultivated Areas/Soils (0.6)  Polluted Water (0.6)  Lakes/Ponds/Reservoirs (No Human Use) (0.628)  Swamps/Marshes/Wetlands/Stagnant Water (0.628)  Intermittently Flooded Areas/Water (0.628)	0.630	NS	NS	8,227,000
Woodland Use Pine Forest/Shelterbelt (0.9375) Eastern White Pine (Forest) (0.9375)	0.94	NS	NS	17,000
Rangelands/Pastures/Set Aside Acreage/Summer Fallow Canarygrass (1.2) Rangeland or Pastures (1.25) Grass Forage/Fodder/Hay (1.25)	1.25	NS	NS	1,625,000
Ornamental Plant Uses-Nurseries- Homeowner Ornamental trees and Herbaceous Plants	1.746	NS		175,000
Ornamental Nonflowering Plants Ornamental Woody Shrubs and Vines (2.5)	2.50	NS	NS	
Commercial Tree Production Christmas Tree Plantations, (3.125) Ornamental and/or Shade Trees (3.125) Slash Pine (forest) (3.125)	3.125	NS	NS	No estimate provided
Public Parks	_			67,000
Turf Use/ Golfcourses/Commercial Lawncare Ornamental Lawns and Turf	5.1	NS	NS	35,000 (golfcourses + cemeteries) Commercial landscape= no estimate provided
T-4-1 N-1 A - 11-1 11 A 100 0	00.11	/LICED A	ODD/DE A	D (' ( )

Total Non-Ag Use per Year-4,100,000 lbs ai/year (USEPA OPP/BEAD estimates)

NS=Not Specified

# **Exposure Characterization**

## **Environmental Fate and Chemistry of Malathion**

#### A. Chemical Profile

## O,O-Dimethyl phosphorodithioate of diethyl mercaptosuccinate

## Physical/Chemical properties:

Molecular formula:  $C_{10}H_{19}O_6PS_2$ . Molecular weight: 330.3 g/mol.

Physical state: Clear amber liquid.

Melting point: 2.85° C. Boiling point (0.7 mm Hg): 156-157° C.

Specific gravity (25° C): 1.23

Vapor pressure  $(30^{\circ} \text{ C})$ :  $4 \times 10^{-5} \text{ mm Hg.}$ 

Solubility (25°C): 145 mg/l water.

## **B.** Environmental Fate Summary

Wildlife and humans may be exposed to malathion and its degradates through contamination of food, water, and air (by suspended particles) which can result from off-target drift, runoff, and direct application. Increased toxicity may be brought about through oxidation (to malaoxon) and isomerization (to isomalathion). Limited data is available on toxic degradates and impurities, but the fate data on malathion is acceptable and shows little persistence. Based on registrant data and open literature reports, EFED concludes that the primary route of dissipation of malathion in surface soils appear to be microbially mediated soil metabolism (half-life <1-2.5 days) and hydrolysis (pH 7 half-life 6.21 days and pH 9 half-life 12 hours) with malathion monoester, ethyl hydrogen fumarate, diethyl thiosuccinate, malathion mono- and dicarboxylic acids, demethyl mono- and dicarboxylic acids, and CO<sub>2</sub> as known degradates.

Other important routes of dissipation from soil suggested by the data include leaching, plant uptake, and surface runoff. Malathion and its degradates in general are soluble and do not adsorb strongly to soils. Data from the field dissipation studies indicate that malathion dissipates rapidly

when applied in the field. Although the anaerobic and aerobic aquatic metabolism and aquatic field dissipation studies indicate very rapid degradation ( $T_{1/2} = <2.5 \text{ days}$ ), the metabolism studies were performed under alkaline conditions that favor hydrolysis and the water pH in the dissipation study was not specified. As such it is difficult to separate out the effect of hydrolysis from metabolism.

Malathion is stable to hydrolysis at pH 5 ( $T_{1/2} = 107$  days), to aqueous photolysis ( $T_{1/2} = 94$  and 143 days, corrected for dark control) and soil photolysis ( $T_{1/2} = 173$  days) and does not volatilize appreciably ( $\leq 5.1\%$  of applied volatilized after 16 days). Open literature studies suggest persistence on soil is longer under dry, sandy, low nitrogen, low carbon, and acidic conditions (Walker and Stojanovic 1973).

Acceptable leaching data on parent malathion indicate that it is mobile in all soils tested ( $K_ds = 0.82\text{-}2.47$ ). Acceptable terrestrial field dissipation data indicate rapid dissipation ( $T_{1/2} = <2$  days). One detection of malathion below 12 inches was found in a terrestrial field dissipation study, indicating leaching as a likely route of dissipation. Similarly, column leaching studies demonstrated that malathion and its degradates, malathion mono- and dicarboxylic acids are very mobile in soil. Data presented to the Agency and in the "Pesticides and Groundwater Database" (U.S. Environmental Protection Agency 1992) demonstrate that malathion has the potential to leach to ground water. Malathion has been detected in ground water in three states (California, Mississippi, and Virginia) at levels ranging from 0.03 to 6.17 ppb. Based on these data and the low  $K_d$  values for malathion it is clear this chemical has the potential to leach to ground water.

Technical malathion contains impurities that account for up to 5% of the insecticide. California Department of Food and Agriculture (CDFA 1991) has reported 15 impurities present in a representative ultra low volume malathion formulation. These impurities include:

```
diethyl fumarate (0.90%)
diethylhydroxysuccinate (0.05%)
O,O-dimethylphosphorothioate (0.05%)
O,O,O-trimethyl phosphorothioate (0.45%)
O,O,S-trimethyl phosphorodithioate (1.20%)
Ethyl nitrite (0.03%)
Diethyl-bis (ethoxycarbonyl) mercaptosuccinate (0.15%)
S-1,2-ethyl-O,S-dimethyl phosphorodithioate [isomalathion] (0.20%)
S-(1-methoxycarbonyl-2-ethoxycarbonyl)ethyl-O,O-dimethyl phosphorodithioate (0.60%)
Bis-(O,O-dimethyl thionophosphoryl) sulfide (0.30%), Diethyl methylthiosuccinate (1.00%)
S-ethyl-O,O-dimethyl phosphorodithioate (0.10%)
S-1,2-bis (ethoxycarbonyl) ethyl-O,O-dimethyl phosphorothioate [malaoxon] (0.10%)
diethyl ethylthiosuccinate (0.10%)
sulfuric acid (0.05%).
```

Some malathion (and other organophosphate) impurities can potentiate malathion toxicity and also are toxic alone, but there is almost no data available on their environmental fate. The persistence of a phosphorothioate impurity (O,O,S-trimethyl phosphorothioate) was shown to be 18.7 times

longer than malathion in a aerobic soil metabolism study (Miles and Takashima 1991). Some phosphorothioates and -dithioates have been intensively studied and induce a delayed toxic effect to mammals at much lower levels than pure malathion (Ali Fouad and Fukuto 1982, Umetsu *et al* 1977, Fukuto 1983, Aldridge *et al* 1979, Toia *et al* 1980). A phosophorothioate and -dithioate impurity identified by CDFA (1991) are of lower toxicity than impurities reported in older formulations (Toia et al 1980). One hydrolysis product, diethyl fumarate, which is also present as an impurity in technical malathion is approximately 3 times more toxic to fathead minnows than malathion (Bender 1969). No guideline studies have been conducted and little open literature data exist to define the fate and persistence of impurities of malathion, however, most of the highly toxic impurities identified in past studies on malathion (Ali Fouad and Fukuto 1982, Umetsu *et al* 1977, Fukuto 1983, Aldridge *et al* 1979, Toia *et al* 1980) have not been identified or are present only at low levels in more recently produced technical malathion (CDFA 1991 and confidential information provided by the registrant).

The relative concentration of malathion impurities can vary dramatically depending not only on manufacturing processes but also storage conditions. Umetsu *et al* (1977) concluded:

"Storage of technical malathion for 3 to 6 months at 40 degrees C resulted in materials which were noticeably more toxic to mice."

"Needless to say, malathion should not be stored for prolonged periods under conditions where it is subjected to consistently high temperatures."

Thus, the composition and toxicological properties of the technical product are affected by initial quality and storage conditions.

One impurity of malathion is the oxon analog, malaoxon, which is also the active acetylcholine-esterase inhibiting component *in vivo*. Under some dry and microbially inactive environmental conditions malaoxon is formed from malathion at levels up to 10.7% of the total applied (CalEPA 1993). Monitoring studies conducted during medfly control programs show high levels of malaoxon (greater than 328 ppb) in runoff water (CDFG 1988). EFED does not have a complete environmental fate database for malaoxon but based on its chemical similarity to malathion (sulfur is replaced by oxygen), the parent and its degradate are expected to have similar chemical properties. The aerobic half-life of malaoxon has been reported as 3 and 7 days in basic and acidic soils, respectively (Paschal and Neville 1976). This longer half-life relative to malathion is proposed to be a result of malaoxon's biocidal effect on soil microbes which contribute to malathion's degradation.

#### **Requirements**

Data for the aerobic aquatic metabolism studies are considered supplemental at this time. The deficiency of this study is the alkaline pH of the soil and water used. Degradation of malathion is highly pH dependent, with faster rates at higher pH. Thus, a quantitative assessment of malathion fate and persistence under acidic conditions when hydrolysis would be slower cannot be conducted. As a result, EFED cannot complete a quantitative assessment of the environmental fate of malathion and its degradates in acidic environments it is likely to contact. An aerobic metabolism study (162-4) performed under pH conditions that do not favor hydrolysis is

requested as EFED believes this additional information will enable a more quantitative assessment of the fate and persistence of this major use chemical in acidic aquatic environments. This request is especially relevant given the sensitivity of numerous aquatic organisms to malathion.

Although the anaerobic aquatic metabolism study was also conducted under alkaline conditions favoring hydrolysis, EFED believes that hydrolysis data along with open literature data on the persistence of malathion in sediments is sufficient to conclude that malathion will not persist under anaerobic conditions. However, an anaerobic aquatic metabolism study under acidic conditions may be requested if more quantitative data on malathion degradation and degradates is needed.

Fate data is required for malaoxon, the oxidation product of malathion. Malaoxon is commonly believed to be the neuroactive toxic agent of malathion after oxidation *in vivo* and toxicity data show it to have higher acute toxicity than malathion. EFED acknowledges that maximal malaoxon conversion under registrant submitted study conditions was low (1.8%) however under other conditions encountered during malathion use conversion levels as high as 10.7% of applied insecticide have been reported (CalEPA 1993). HED also has indicated that malaoxon is to be included in the tolerance expression for malathion. First tier surface water assessments were performed by making several assumptions about the properties of malaoxon relative to malathion. It is not possible to perform second tier assessments without further information specific to malaoxon; thus, EFED requests data required to predict malaoxon levels in drinking water and aquatic habitats.

In addition to data on the basic physical properties of malaoxon (solubility, partition coefficient, vapor pressure), EFED requests that the following laboratory studies be submitted for malaoxon based on the brief justification provided. Data from these studies are expected to be sufficient to perform basic fate and exposure modeling of malaoxon.

## **Degradation**

161-1 (hydrolysis)

Malathion hydrolysis is an important route of dissipation under alkaline conditions. The phosphorothiolate ester bond of malaoxon may be more susceptible to cleavage via hydrolysis than the analogous phosophorodithioate ester in malathion.

## Metabolism

162-1 (aerobic soil) The primary route of malathion degradation on soil is through aerobic metabolism. An open literature study (Paschal and Neville 1976) suggests malaoxon persistence may be greater on soils. Additionally, CalEPA studies have shown levels of malaoxon production exceeding 10% in certain dry, low organic content soils.

## 162-4 (aerobic aquatic)

Although little or no malaoxon production is observed in registrant submitted aquatic studies malaoxon has been detected in surface waters and the potential for malaoxon runoff may be

heightened relative to malathion because it is expected to have higher solubility. Aerobic aquatic metabolism contributes greatly to malathion degradation.

## **Mobility**

163-1(leaching/adsorption)

EFED is not aware of reports of malaoxon groundwater contamination. However, malathion has contaminated groundwater in several states and has the potential to contaminate surface water through runoff. The increased polarity of malaoxon due to the substitution of oxygen for sulfur increases the expected potential of this chemical to be mobile in soil.

EFED also requests additional information on environmental malaoxon production. Because malathion is used in a large number of settings including more than 60 terrestrial field uses as well as outdoor residential uses including mosquito, Mediterraean fruitfly, and urban pest control uses, it is exposed to a large variety of environmental conditions. This extensive use is likely to result in significant exposure of nontarget organisms to malathion breakdown products. Exposures to humans and wildlife may be through contamination of food, water, and air (by suspended particles) which can result from off-target drift, runoff, and direct application.

It is clear that under many circumstances malathion degrades rapidly to compounds of lower toxicity, usually through microbial metabolism and hydrolysis. However, in residential uses (e.g. aerial and ground application for mosquito control), it is likely that malathion will contact dry, microbially inactive and low organic content surfaces such as concrete, asphalt, dry soil, roofing material, and glass. It is expected that malaoxon production will be increased on these surfaces as malathion is exposed to air for extended periods until it is washed away by rain. This is supported by malaoxon monitoring data in urban streams after residential malathion treatment showing similar or higher levels of malaoxon than malathion in some instances (State of California Department of Food and Agriculture, 1982). Thus EFED proposes that malathion persistence and degradation on anthropogenic surfaces be examined (suggestions from the registrant are invited for particular surfaces to be examined). The State of California EPA has published two studies describing adequate methods for determining malaoxon production on dry soil (CalEPA 1993) and steel sheets (CalEPA 1996) which would be amenable to other abiotic surfaces. Both of these studies showed higher malaoxon production than registrant submitted studies, but maximal levels of malaoxon production were not achieved. On the steel surface a rainfall event removed most of the malathion after only 2 days. On the dry soil malaoxon production did not decrease by the time the study was terminated at 22 days. Runoff of residential malathion and malaoxon greatly increases risk of human and aquatic wildlife exposure through drinking water and habitat contamination and increases the need for this information.

The State of California EPA has published a study describing malaoxon production on low organic content soil (0.6%) with a moisture content less than 1% (CalEPA 1993) showing higher malaoxon production than registrant submitted studies using soils with higher organic (2-2.7%) and moisture (75% of water holding capacity, capacity not stated) content. From the CalEPA data it appears that malaoxon production is favored on dry soils and thus may represent a higher

risk scenario for malaoxon production and runoff. EFED believes that data on dry soils may be useful to assess malathion and malaoxon fate and persistence in some use settings which are not ideal for malathion degradation, thus EFED requests the submission of data on malathion degradation and malaoxon production in an aerobic soil metabolism study (162-1) using a soil with a low moisture content (<1%) and low organic content (<1%).

## Conclusions

Malathion is generally nonpersistent, however EFED lacks important information to evaluate the behavior of malathion under acidic aquatic conditions which might likely increase its persistence and alter degradates produced. To adequately determine the environmental fate of malathion and its degradates aerobic aquatic metabolism data under acidic soil and water conditions are needed. Data are also required on the oxidative degradate malaoxon. Presently EFED has no registrant submitted fate data for malaoxon. Monitoring data suggest that malaoxon production is an important issue in residential areas. Thus, EFED is requesting studies of malathion degradation and malaoxon production on anthropogenic surface which 1.) make up much of the residential environment, 2.) increase malathion persistence, 3.) increase malaoxon production, and 4.) increase runoff potential. Acceptable data on malaoxon solubility, hydrolysis, vapor pressure, soil metabolism, and aquatic metabolism in conjunction with information on malaoxon production under high risk conditions will aid EFED in predicting environmental malaoxon concentrations for ecological and human health concerns.

## **Environmental Fate and Transport Studies**

# **Degradation**

## **Hydrolysis:**

Several open literature studies (Mulla *et al* 1981, Howard 1991) are consistent with data presented by the registrant showing that malathion is unstable under alkaline conditions and increasingly stable under acidic conditions. Hydrolysis products characterized by the registrant and in the open literature are similar as well. Muhlman and Shrader (1957) report primary products of diethyl fumarate and dimethyl phosphorodithioic acid in base while the registrant's study identifies malathion monocarboxylic acid and ethyl hydrogen fumarate. The reported differences are relatively minor as ethyl hydrogen fumarate is an expected hydrolysis product of diethyl fumarate and the other products are also expected.

In the registrant's study [14C]malathion was hydrolytically stable in aqueous buffered pH 5 (half-life = 107 days) solutions. At pH 7 and 9 solutions malathion hydrolyzed relatively rapidly with half-lives of 6.21 days and 12 hours, respectively. Parent malathion accounted for 80.3% and 3.7% of applied after 28 days in the pH 5 and 7 solutions, respectively; while after 53 hours of hydrolysis at pH 9, only 3.6% of applied was parent malathion.

The hydrolysis data requirement is satisfied. (MRID 40941201, 43166301)

#### **Photodegradation in water:**

Open literature reports and registrant submitted data suggest that photodegradation in natural and distilled water is relatively slow. Open literature half-life data ranges from 0.67 (natural river water) to 42 days (distilled water) (Howard 1991).

In the registrant submitted aqueous photolysis study,  $[2,3^{-14}C]$  malathion degraded with calculated half-lives (corrected for dark control degradation) of 94 and 156 days in sterile pH 4 photosensitized (1% acetone) and nonsensitized aqueous buffer solutions, respectively, that were irradiated continuously with a xenon arc lamp at  $25 \pm 1$  °C for 30 days. Detections of monoethyl maleate, diethyl maleate, malaoxon, mono-acid, diethyl mercaptosuccinate, and diethyl fumarate were noted at concentrations <<10% of applied.

The photodegradation in water data requirement is satisfied. (MRID 41673001, 43166301)

## Photodegradation on soil:

Registrant and open literature data suggest malathion is stable under sunlight. Open literature on photodegradation of malathion in thin films on glass showed production of 6 degradates but at a maximum level of 0.01% after 16.5 hours (Chukwudebe *et al* 1989).

In the registrant submitted soil photolysis study,  $[2,3^{-14}C]$  malathion degraded with a registrant-calculated half-life of 173 days. The soil used was a pH 6.5 sandy loam. No degradates at concentrations  $\geq 10\%$  were observed. Thus, soil photolysis is not an important route of dissipation for malathion.

The photodegradation on soil data requirement is satisfied at this time (MRID 41695501, 43166301), but EFED requests that the registrant provide an explanation for the long persistence of malathion in irradiated and dark control samples. Soils were stated to possess microbial activity which would lessen persistence making it unclear why malathion was stable under the study conditions.

#### Photodegradation in air:

The relatively low vapor pressure of malathion suggests gas phase reactions are only minor routes of degradation. However, malathion in the form of very small droplets ( $\sim 10 \, \mu m$ ), such as might result from ULV formulation application, may reach much higher concentrations in air. No open literature references on photodegradation in air were found.

In a the registrant supported photolysis in air study, >10% [2,3-<sup>14</sup>C]malathion, contained in Tedlar bags, degraded during 4 days of irradiation. The photolysis in air data requirement is not satisfied, however, EFED agrees with the registrant that the study should not be required for several reasons. In the laboratory volatility study, less than 5% of malathion was volatilized from soil surfaces, indicating that obtaining a significant vapor flux that can be experimentally studied for true vapor photolysis is inherently difficult. In addition, the UV absorption spectrum of malathion shows an onset of absorption at about 260 nm, well below the 290 nm cutoff for natural sunlight irradiation and for the xenon light source used in the study. Thus, photodegradation of malathion in air is not expected. This conclusion is also supported by the lack of photodegradation in either the aqueous photolysis or the soil photolysis studies. Finally, as noted in the Rejection Rate Analysis (EPA 1993), this study often generates data that are difficult to interpret, and EPA has dramatically reduced the instances in which this study is required.

## Metabolism

#### **Aerobic Soil Metabolism:**

Aerobic soil metabolism is an important route of malathion degradation. Malathion persistence under aerobic soil conditions has been examined in several open literature studies which are reviewed in Table 3. Reported half-life values (from field and laboratory studies) vary from hours to 11 days. Persistence is decreased with microbial activity, moisture, and high pH.

Table 3.

Source	Degradation Rate Value	Comments
Miles and Takashima 1991	$t_{\frac{1}{2}} = 8.2 \text{ h (laboratory)}$ $t_{\frac{1}{2}} = 2 \text{ h (field)}$	malathion was mixed with Lihue soil and incubated at 22°C in lab experiment. Sterilization decreased rate 2-fold.
Walker and Stojanovic 1974	47-95% at 7 days	malathion was incubated with various <i>Arthrobacter</i> species.  Degradation in the presence of the 5 most efficient species was reported.
Walker and Stojanovic 1973	t 1/2 = ~ 2 days under non-sterile unfavorable degradation conditions.	Three Mississippi soils were examined at 25-26°C. Soil microflora were important in degradation. Slowest degradation occurred in soils with low nitrogen, moisture, carbon content and increased acidity.

CalEPA 1994	DT50 = 4.2-6.9 days on sand	Measured at five sites under the conditions of the medfly eradication program. Each site consisted of 10 aluminum trays containing 500g of playgound sand. Between applications trays were covered.
CalEPA 1993	DT50 < 12 h on sand	Application was under controlled conditions but temperature was not noted.
CalEPA 1993	soil: 38% remaining at 12 hours 15% remaining at 20 days	66% sand, 24% silt, 10% clay, 0.78% water, pH 6.3. Malathion was applied under controlled conditions. Degradation was biphasic.
Kearney et al 1969	75-100% degradation in 1 week	Field persistence
Lichtenstein and Schultz 1964	85% dissipation in 3 days	Conducted under field conditions
Handbook of Environmental Fate and Exposure Data for Organic Chemicals 1991	Reported average literature $t_{1/2} = 6 d$	In this review persistence is stated to vary with moisture content and pH.
USDA	$t_{1/2} = 3$ days used for modeling	This value was chosen for modeling malathion in the boll weevil eradication program based on a personal communication with a previous malathion registrant.

In the registrant submitted study [2,3- $^{14}$ C]malathion degraded with a calculated half-life of approximately 0.2 days in two aerobic metabolism experiments using loam soil (pH 6.1) incubated in the dark at  $22 \pm 2^{\circ}$  C and 75% of field capacity. An ancillary experiment was conducted to determine the rate of degradation of malathion in sterile soil. At 4 days posttreatment, malathion comprised close to 100% of the applied radioactivity (97.84% of the extractable radioactivity). This indicates that microorganisms are important in the rapid degradation of malathion in soil under acidic aerobic conditions (MRID 41721701, 43166301).

Numerous degradates were identified in the soil extracts and are identified below as a percent of applied radioactivity: dicarboxylic acid of malathion-18.7-36.7%, the beta monocarboxylic acid of malathion-2.8-7.3%, the alpha monocarboxylic acid of malathion-1.9-2.5%, and malaoxon-0.6-1.8%.

Soil bound (unextracted) residues averaged 32% of applied at the 6 hour sampling, which increased to 65% at the 24 hour samples and then slowly decreased to 39% after 92 days of incubation. Total  $^{14}\text{CO}_2$  evolution was 45-56% of the applied radioactivity; while volatile organic residues were  $\leq 0.2\%$ .

The aerobic soil metabolism require is considered satisfied (MRID 41721701, 43166301).

## **Anaerobic Aquatic Metabolism:**

A open literature study (Bourquin 1977) and the registrant's study suggest that malathion persistence in anaerobic environments is short, however, due to the high pH in the registrant's study a quantitative assessment of the degradation and degradation products cannot be performed.

In the registrant submitted anaerobic aquatic metabolism study [2,3-14C]- and technical grade-malathion added to a sandy loam soil degraded with a registrant-calculated half-life of approximately 2.5 days in sediment (pH 7.8) and water (pH 8.7). This study provides useful information, but hydrolysis was probably the main route of degradation in the study since the pH of the system was in the basic range which favors hydrolysis. Although most of the residues remained in the water phase (less than 20% of the applied radioactivity was associated with the soil at any sampling interval), the degradation products were similar in both sediment and water phases. The degradation products at maximum concentrations in the water phase were the monocarboxylic acid of malathion (MCA, 28% at Day 4), demethyl monocarboxylic acid (21% at Day 7), dicarboxylic acid (21% at Day 14) and the demethyl dicarboxylic acid metabolite (39% at Day 45). The degradation products at maximum concentrations in the sediment were the monocarboxylic acid of malathion (4.5% at 6 hours), demethyl monocarboxylic acid (8.1% at Day 45), and dicarboxylic acid (5.2% at Day 4). The EFED calculated half-life for malathion monocarboxylic acid was 11 days.

This study is considered satisfactory with supporting hydrolysis and open literature data suggesting that malathion is unlikely to persist in anaerobic aquatic conditions (MRID 42216301, 43166301). Repeated studies under acidic conditions may be requested if more quantitative data on malathion persistence in these environments are required.

#### **Aerobic Aquatic Metabolism:**

A USGS monitoring study (1998) shows detections of malathion in large rural and urban streams. Many open literature studies have been conducted on the fate and persistence of malathion in the aquatic environment. Reported degradation rates vary and are likely to be significantly increased by biodegradation and pH. Eichelberger and Lichtenberg (1971) found 75% and 90% degradation in river water in one and two weeks, respectively. Guerrant et al (1970) found malathion half lives in pond, lake, river and other natural waters varied from 0.5 to 10 days and was dependent on pH. Other studies are summarized in Mulla *et al* (1981) and Howard (1991).

Registrant submitted studies were conducted under alkaline conditions which favor hydrolysis. Thus, degradation rate and products may be not be representative of acidic aquatic conditions. In the registrant submitted aerobic aquatic metabolism study, a mixture of [2,3-<sup>14</sup>C]- and technical grade-malathion added to a sandy loam soil rapidly degraded in the aerobic aquatic environment with a half-lives of approximately 1.09 days in the water phase (pH 7.8) and 2.55 days in sediment

(pH 8.5). As mentioned above, hydrolysis was probably the main route of degradation in the study since the pH of the system was in the basic range and hydrolysis occurs most rapidly at pH 9. Major degradates in water and soil were similar: mono- and dicarboxylic acids of malathion, demethyl monoacid and demethyl diacid, while in sediment no demethyl diacid was detected. The EFED calculated half-life for malathion monocarboxylic acid was 3 days.

This study is considered supplemental at this time (MRID 42271601, 43166301) as quantitative data for malathion degradation in acidic aquatic environments where it is likely to have longer persistence are required. Malathion's high toxicity to aquatic animals and the need to model malathion fate for drinking water assessments in a conservative manner are two important aspects of this assessment which directly rely upon quantitative aquatic fate data.

# **Mobility:**

## **Leaching/adsorption/desorption:**

The short soil persistence of malathion reduces the risk of leaching to groundwater however it has been detected in the groundwater of at least three states (USEPA 1992). Demethyl and carboxylic acid degradates are expected to be highly mobile particularly in alkaline soils.

Based on batch equilibrium (adsorption/desorption) studies, unaged [ $^{14}\mathrm{C}$ ]malathion was determined to be very mobile in sandy loam, sand, loam, and silt loam soils, with respective Freundlich  $K_{ads}$  values of 0.83-2.47; and  $K_{oc}$  values from 151-183. Adsorption was correlated with organic carbon content. Values for 1/n for  $K_{ads}$  were clustered in the range of 0.904-0.978 (MRID 41345201).

Malaoxon was detected in any leachate or soil extracts in concentrations  $\ge 0.12\%$  ( $\ge 6$  ppb) of applied radioactivity. (MRID 43868601, 41345201, 43166301)

## Laboratory volatility:

Three different malathion formulations [Ready To Use (RTU), Ultra Low Volume (ULV), Emulsifiable Concentrate (EC)] added to a silt loam soil did not undergo any appreciable volatilization, when measured under different soil moisture regimes or air flow rates. No more than 5.1% of the applied radioactivity volatilized during the 16 days of the study.

# Dissipation

#### **Terrestrial field dissipation:**

Open literature studies provide varying rates of terrestrial dissipation. Mulla *et al* (1981) summarizes degradation results from several field studies including: no residues after 6 months (Roberts *et al* 1962), and 85% degradation in 3 days and 97% in 8 days (Lichtenstein and Schulz

1964). The fastest route of terrestrial field dissipation is generally accepted to be via microbial degradation.

In the registrant submitted field dissipation study using a rate of 1.16 lb ai/A, malathion or malaoxon residues were detected at  $\leq$ 10 ppb in the 0-6" layer in cotton/bareground sites in GA. Due to the sampling depth it is not possible to determine how much malathion remained at the soil surface relative to that which moved through the first six inches. Residues detected in the plots in the 6-12" layer after the 2nd, 3rd, 4th and 5th treatments averaged 35, 37, 5.6 and 9.4 ppb, respectively. Malathion was detected in the 12-18 inch soil depth at 16 ppb in one replicate soil sample; however, the detection was attributed to contamination. The detection of malathion below six inches along with the low  $K_d$  values reported for malathion make it feasible that leaching below 12 inches may have occurred in the field dissipation studies.

The half-life could not be determined due to the rapid dissipation of malathion, although it is probably <1 day (MRID 41748901, 43042401, 43166301).

In a field dissipation study located in California, malathion was applied at a maximum rate of 1.16 lb ai/A once a week for 6 weeks. The resulting dissipation half-life was <0.2 days. In certain instances, malathion was detected below the 12 inch soil depth (MRID 41727701, 43042402, 43166301).

## Aquatic field dissipation:

Open literature references detailing persistence in aquatic environments are briefly mentioned under the aquatic metabolism section.

In the first registrant aquatic field dissipation study located in Missouri, malathion was applied at a maximum rate of 0.58 lb ai/A in three weekly applications to a flooded rice paddy (soil pH 6.1, water pH not stated). Malathion residues detected in water samples collected after the first and second application had dissipated below the detection limit (0.01 ppm) in samples taken prior to the second and third applications. In water samples collected one day after the last application, malathion concentrations averaged 0.017 ppm and had decreased to <0.01 ppm by the second sampling day. Malaoxon residues were <0.01 ppm at all sampling dates.

The data indicate a very rapid dissipation of malathion in water, probably <1 day; however, an accurate half-life could not be determined because of the rapid dissipation (MRID 42058402, 43166301).

In the second aquatic field dissipation study performed in California (soil pH 7.4, water pH not stated), malathion was applied at a rate of 0.58 lb ai/A in three weekly applications to flooded plots. The resulting dissipation half-life could not be determined in the California plot because it was probable that only 1-2% of the intended amount of malathion was applied (MRID 42058401, 43166301).

## **Accumulation**

#### **Accumulation in irrigated crops:**

Crop accumulation and residue studies are conducted under the purview of the Health Effects Division. In an accumulation in irrigated crops study located in Missouri, which used the irrigation water from the above mentioned aquatic field dissipation study on rice, malathion or malaoxon did not accumulate in corn, grain sorghum, soybeans or sweet potatoes. The study was unacceptable mainly because the authors did not attempt to determine residues in plants, other than malathion and malaoxon, which were detected in laboratory studies. (MRID 42058402, 43166301).

#### **Accumulation in fish:**

Aquatic bioconcentration values ranging from 7.36 (lake trout), 29.3 (coho salmon), 869 (white shrimp), to 959 (brown shrimp) are summarized in Howard (1991).

The registrant submitted study shows [\frac{14}{C}]malathion residues did not significantly accumulate in bluegill sunfish exposed to 0.99 ppb [\frac{14}{C}]malathion in a flow-through system for 28 days. Average concentrations of malathion were 3.9 to 18 ppb in the edible fish parts, 21 to 130 ppb for whole fish and 34 to 200 ppb in the nonedible tissue. [\frac{14}{C}]malathion residue equivalents in the edible fish tissue during depuration ranged from 18 ppb at the start to 4.8 ppb by day 14. Whole fish concentrations decreased from 110 to 4.5 ppb and non-edible fish concentrations decreased from 150 to 5.8 ppb after day 14. Approximately 73, 96 and 96% of the radioactivity depurated from the edible, whole and nonedible portions of fish, respectively. The non-depurated radioactivity consisted of up to 22 other components present in concentrations <10% of total applied radioactivity and were not further identified.

The only significant residue detected in fish tissue was malathion monocarboxylic acid (MCA) in concentrations of 33.3-35.9% (44.8-61.2 ppb) of total radioactive residues (TRR). Up to 22 other components were present in levels of 0.1 to 5.7% (0.1 to 7.7 ppb) and included malathion dicarboxylic acid (MDCA), malaoxon, desmethyl malathion, monoethylfumarate and oxalacetic acid. Malaoxon was present in concentrations  $\leq$ 2.7 ppb; while parent malathion was present in concentrations of 0.2 ppb.

Maximum BCFs, as a function of radioactive residues present, ranged from 4.2 to 18, 23 to 135, and 37 to 204 for edible, whole fish and nonedible, respectively (MRID 43106401, 43106402, 43340301).

# **Spray Drift**

No registrant-submitted spray drift studies were reviewed. A study conducted for the Boll Weevil Eradication Program at Penn State (1993) examined malathion drift under conditions of

boll weevil control (1 lb/A =  $112 \text{ mg/m}^2$ ) with an ultra-low volume (ULV) formulation. Deposition up to 21.0, 11.5, 2.9, and 0.7% of that applied was observed at 100, 200, 500, 1000 meters downwind. Due to the size of the particles generated, the ULV formulation is expected to produce the highest levels of drift.

To satisfy spray drift study requirements the registrant, in conjunction with other registrants, formed the Spray Drift Task Force (SDTF). The SDTF has completed and submitted to the Agency its series of studies which are intended to characterize spray droplet drift potential due to various factors, including application methods, application equipment, meteorological conditions, crop geometry, and droplet characteristics. During 2000 EPA plans to complete the evaluation of these studies. In the interim and for this assessment of malathion, the Agency is relying on previously submitted spray drift data and the open literature for off-target drift rates. The simplified rates used are 1% of the applied spray volume from ground applications and 5% from aerial and orchard airblast applications at 100 feet downwind. It is important to note that drift studies on ULV malathion show significantly higher levels of drift. After its review of the new studies, the Agency will determine whether a reassessment is warranted of the potential risks from the application of malathion to nontarget organisms.

The status of the environmental fate data requirements for malathion for terrestrial food crop, terrestrial feed crop, indoor non-food, and residential outdoor uses is summarized in the appendices.

## C. Terrestrial Exposure Assessment

#### **Terrestrial Vegetation Exposure**

## Exposure Concentrations for Nontarget Terrestrial Wildlife and Insects

For pesticides applied as a nongranular product (e.g., liquid, dust), the estimated environmental concentrations (EECs) on food items following product application are compared to LC50 values to assess risk. The predicted 0-day maximum and mean residues of a pesticide that may be expected to occur on selected avian or mammalian food items immediately following a direct single application at 1 lb ai/A are tabulated below.

Table 4

Food Items	EEC (ppm) Predicted Maximum Residue <sup>1</sup>	EEC (ppm) Predicted Mean Residue <sup>1</sup>
Short grass	240	85
Tall grass	110	36
Broadleaf/forage plants, and small insects	135	45
Fruits, pods, seeds, and large insects	15	7

<sup>&</sup>lt;sup>1</sup> Predicted maximum and mean residues are for a 1 lb ai/a application rate and are based on Hoerger and Kenaga (1972) as modified by Fletcher *et al.* (1994)

## Residues on Vegetation from Multiple Applications

Predicted residues (EECs) resulting from multiple applications are calculated in various ways. The Agency has employed simple first order dissipation calculations to predict concentrations on vegetative surfaces following spray application at 0.18 to 6.25 lbs ai/acre. The application scenarios are based on maximum tested rates, minimum intervals and maximum numbers of applications tested for establishment of residue tolerances on food. An assumed 90th percentile foliar dissipation half-life of 5.5 days on plant surfaces was derived from averaging of calculated half lives based on 37 reports of malathion residue samples collected on 12 different crops by various researchers from 1957 to 1981 as reported in Willis and McDowell, 1987 (see table below).

Table 5 a . Foliar Halflife Estimates for Malathion -Willis and McDowell

Crop(# samples) Formulation types	Location	Rainfall in mm	Half-life in days
Alfalfa(3) Dust & EC	NC, MA	6.1 to 17.8	0.7, 2.0, and 4.1
Apple(1)	WA	Not reported	$3.2 \pm 1.2$
Chicory(3) Dust, EC, & WP	MD	0	0.7, 0.8, and 1.4
Collards(4) Dust, WP, & EC	NC, MD	0	1.0, 1.4, 1.5, and 1.7
Cotton(5) EC	KY, MS	Not reported	0.3, 0.4, 1.1, 0.6, 6.1
Citrus(1)	FL	Not reported	2.3
Endive(3) Dust, WP, & EC	MD	48.8	1.2, 1.5, 5.9
Leaf lettuce(3) Dust, WP, & EC	MD	0	2.9, 5.8, 6.8
Lima Beans(3) ULV, oil mix	MD	Not reported	1.3, 2.5, 2.8
Kale(1) EC	DC	Not reported	3.1
Turnip(1) EC	FL	60.7	6.4 <u>+</u> 2.7
Tobacco(8) Dust, WP, & EC	MD	0.8 to 16.0	0.7, 0.7, 1.7, 2.1, 2.4, 2.8, 3.2, 10.9

Based on this foliar dissipation data and resulting residue calculations a table has been developed with food tolerance scenarios as guidance in predicting maximum expected surface residue ranges for terrestrial vegetation and insects. Single application residues ranged from 42 to 1500 ppm on short grass coresponding with application rates which range from 0.175 to 6.25 lb ai/A. The range on seeds and fruit pods ranged from 1.2 to 42 ppm for the same single application scenarios. Multiple application residue ranges on shortgrass ranged from 72 to 1900 ppm for rates that range from 0.175 (10 applications) to 6.25 lbs ai/A (3 applications). Use of 7 day or

greater intervals does appear to reduce the aggregate increase in residue levels and some equilibrium occurs. Refer to Table 5b in the appendix 5 for predicted residues for each crop use scenario for malathion supported crops.

The estimates of residues used in table 5b are not highly conservative as calculated foliar dissipation half lives were as high as 10.9 days in the Willis and McDowell report. A slight increase in residues is predicted from multiple applications.

Johansen *et al* (1965) conducted a study entitled Bee Poisoning Hazard of Undiluted Malathion Applied to Alfalfa in Bloom. Foliar residues were measured during this study, which is also referenced in the hazard portion of this document under non-target insect toxicity field studies. The malathion residues appeared relatively stable on surfaces of alfalfa foliage for the first 4 days. It appears that washoff may have led to significant reduction of residues on vegetative surfaces. Degradation appeared marginal before the rainfall events. (See table 6 in appendices for actual values).

Awad et al (1967) conducted a study entitled The Effect of Environmental & Biological Factors on Persistence of Malathion Applied as Ultra Low Volume or Emulsifiable Concentrate to Cotton Plants. In the study small amounts of insecticide were applied to plant surfaces and glass plates. Samples were taken at application and 1, 3, 6 & 9 days post application. Malathion EC and ULV formulations were used. Residues were obtained by washing leaves or plates with 100 ml of distilled water. EC formulations appeared to penetrate leaf tissues more rapidly than ULV formulations. Lack of absorption led to higher residue levels on glass plate surfaces. Calculated foliar half lives were ULV T1/2 = 5.5 days and EC T1/2 = 23 days.

#### D. Water Resource Assessment

The highest level of malathion surface water contamination occurs in urban areas. Malathion deposited on anthropogenic surfaces decays slowly and is more likely to be washed off to adjacent water bodies. Agricultural uses of malathion are most likely to contaminate surface water through off-target drift. This is particularly true with aerially-applied, drift-prone ULV formulations.

Malathion contamination of ground water has been observed at higher levels than predicted by modeling. Malathion ground water contamination is surprising given its rapid degradation under most conditions and emphasizes the need for data requested on malathion fate under conditions which do not favor degradation.

EFED uses a tiered system to generate estimates of pesticides in surface and groundwater. First tier assessments utilize the simple farm pond model GENEEC and reviewed monitoring studies. Second tier assessments are intended to reduce the uncertainties of first tier assessments and produce more realistic estimates of pesticide concentrations. Second tier assessments utilize PRZM-EXAMS modeling and a more comprehensive review of available monitoring data.

Water assessments used in this document examine both malathion and when possible its toxic degradate malaoxon. Technical malathion contains, in addition to malaoxon, other impurities that are demonstrated to be toxic or to synergize malathion toxicity. These chemicals include isomalathion and alkyl phosphorothioates and -dithioates. These impurities are normally present individually at levels less than 1% but can increase under improper storage conditions. As EFED possesses very little environmental fate data on these impurities it is not possible to assess their fate or persistence in the environment through modeling. Therefore an assessment of malathion impurities in water is not included in this document.

## 1. Drinking Water

A first tier drinking water assessment has been performed to provide the Health Effects Division with a conservative estimate of malathion and malaoxon in drinking water. Acute and chronic drinking water concentrations were estimated with proposed pesticide use patterns that produced the highest aqueous pesticide levels. The model results reflect first tier drinking water concentration estimates and environmental concentrations as a result of agricultural use. HED has indicated that malathion's degradate, malaoxon, is to be included in the tolerance expression for malathion. Thus, water concentrations are provided in this assessment for both malathion and, when possible, malaoxon. The results are summarized in the table below. A more detailed discussion is provided in the discussion on ground water and the memo sent to HED is included in the appendices.

Table 7. Tier I drinking water concentrations for malathion and malaoxon.

compound /	surface wate	r	gı	round water	
exposure type	estimated concentration (ppb)	source of concentration	estimated concentration (ppb)	source of concentration	
malathion / acute	226	GENEEC peak			
malathion / chronic	21.2	GENEEC 56-day ave.	3.1	Monitoring data	
malaoxon / acute	96.0	GENEEC peak		Derived from malathion	
malaoxon / chronic	75.5	GENEEC 56-day ave.	3.1	monitoring data	

EFED recommends that 226 and 96.0 ppb (Table 7) be considered as the highly conservative first tier estimates for acute surface drinking water levels for malathion and malaoxon, respectively.

For chronic surface drinking water levels, 21.2 and 75.5 ppb are recommended for malathion and malaoxon, respectively. The chronic malaoxon value exceeds the chronic malathion level because of its longer expected environmental persistence.

First tier groundwater concentrations were derived from monitoring data because they were higher than results from the SCIGROW model (0.142 ppb for cotton). The highest detected malathion concentration in groundwater accepted by EFED was 3.1 ppb. Malaoxon was not examined in this monitoring study, but the same value is expected to be a conservative estimate of malaoxon concentration as malaoxon production usually accounts for less than 10% of malathion degradates. EFED recommends exposure estimates of 3.1 ppb for malathion and 3.1 ppb for malaoxon in ground water.

Standard modeling techniques were modified to estimate malaoxon concentrations. Malaoxon levels were estimated with the GENEEC model with the <u>assumption</u> that fate variables which were not known are the same as those for malathion. Acceptable environmental fate studies specifically for malaoxon; including degradation, metabolism, mobility, dissipation, and solubility data; are needed for a complete assessment.

EFED notes that there is limited information available on the conversion of malathion to malaoxon during drinking water treatment. Available data suggest that conversion of malathion to malaoxon may be more efficient during water treatment than under natural conditions in the field, thus malaoxon may be present at a much higher concentration relative to malathion after water processing.

In a limited sampling of water entering and leaving a water treatment plant in Florida both malathion and malaoxon levels generally decreased after treatment, however, one sample showed an increase in malaoxon (USDA 1997). Data from a more detailed sampling and analysis with a lower detection limit show a much higher rate of conversion (personal communication, Dr. Marion Fuller, Florida Department of Agriculture and Consumer Services).

Data supplied by the Florida Department of Agriculture and Consumer Services Bureau of Pesticides provides malathion concentrations entering and leaving the Hillsborough Water Treatment Plant during the period of July 16 - August 27 1997. At this time the area was being sprayed with baited malathion for medfly control. The reservoirs and other known sources of drinking water reportedly did not receive direct insecticide treatment. Samples were collected at a boat dock prior to entering the plant and as well as after treatment. Table 8 summarizes the data.

**Table 8**. Drinking water entering and leaving the Hillsborough Water Treatment Plant 1997. Detection limits were 0.1 ppb for both malathion and malaoxon.

Malathion-malaoxon conversion in water treatment										
location	malathion (average of detected concentrations, ppb) <sup>1</sup>	s.d dev.	n	malaoxon (average of detected concentrations, ppb) <sup>1</sup>	s.d dev.	n				
Boat dock	1.00	0.90	13	nd	-	25				
Lab/Finished	nd	-	25	1.09	0.73	14				

These results suggest that the water treatment process can result in a very efficient conversion of malathion to its oxon. It is likely that the efficiency would vary depending on the type of water treatment process used in sterilization. The stability of malaoxon in the drinking water supply cannot be assessed as EFED does not presently possess hydrolysis data on malaoxon. Therefore it is assumed to be stable in drinking water.

#### 2. Estimated Concentrations for Surface Water Resources

#### **Tier I Assessment**

## Summary

Based on fate characteristics, model predictions and actual monitoring studies, the Agency predicts malathion will reach surface and groundwater water from the proposed reregistration uses. Surface water concentrations resulting from agriculture uses were modeled using the GENEEC screening model. Results are presented in the following table.

 Table 9. GENEEC Predicted Environmental Concentrations For Aquatic Exposure

 Estimated Aquatic EECs in PPBs:
 Peak (top), 21 day mean (middle), and 56 day mean (bottom).

							er of App		udie), and .	·	·	·	
	Rate lb ai/A	Int. Day	1	2	3	4	5	6	7	8	9	10	12- 25
A	0.175	7D										8.24 2.03 0.78	
В	0.50	NA	11.4 2.8 1.07										
С	0.61	7D		23.2 5.7 2.2	27.7 6.8 2.6								
С	0.61	14D		26.8 6.6 2.53									
D	0.76	10D					40.6 10 3.4						
E	0.94	3D	21.7 10.4 2.05										
E	0.94	6D						45.4 11.2 4.24					
E	0.94	7D			42.2 10.4 3.94				42.5 10.5 3.97				
F	1.0	7D						45.2 11.2 4.22					
G	1.25	3D	28.5 7.0 2.66	54.3 13.4 5.07				90.4 22.3 8.5					
G	1.25	5D					66 16.3 6.16						
G	1.25	7D			56.1 13.8 5.24	56.5 13.9 5.3	56.5 13.9 5.28	57.2 14.1 5.4	56.5 13.9 5.28	56.6 13.9 5.28	56.6 13.9 5.28	56.6 13.9 5.28	56.6 13.9 5.28
G	1.25	14D		47.1 11.6 4.53									
Н	1.50	7D			67.3 16.6 6.28			67.3 16.6 6.28					

	lb ai/A	Int. Day	1	2	3	4	5	6	7	8	9	10	12- 25
Ι	1.56	7D		67.8 16.7 6.33			70.8 17.5 6.61						
J	1.88	5D						99.4 24.6 9.28					
J	1.88	7D			84.4 20.8 7.87	84.9 21 7.92		85 21 7.94					
J	1.88	14D		70.8 17.5 6.61									
K	2.03	6D						98.1 24.2 9.16					
K	2.03	7D			91.1 22.5 8.5	91.7 22.6 8.6							
L	2.5	3D											181
L	2.5	5D			128 31.6 12								
L	2.5	7D			112 27.7 10.5		113 27.9 10.6						
М	3.43	5D					81 20 16.9						
N	3.75	7D				169 41.7 15.8		169 41.7 15.8					
N	3.75	14D				142 35 13.2							
О	4.7	30D		171 42.2 15.9									
P	5.0	7D			224 55.3 20.9	225 55.6 21.1							
Q	6.25	Q1			226 55.8 21.2								

0.50 lb ai/A **B1**=Flax 0.61 lb ai/A C5(5D)=Sweet Corn, C2(7D)=Hops, C3(7D)=Beans, Corn, Rice, Sorghum, Wheat, C2(14D)=Alfalfa, Clover, Lespedeza, Lupine and Vetch 0.76 lb ai/A **D5**=Blueberry 0.94 lb ai/A E1(3D)=Grass for hay, E4(3D)=Mushroom, E6(6D)=Strawberry, E3(7D) =Peppermint and spearmint, E7(7D)=Macadamia 1.0 lb ai/A **F6(7D)**=Melons, Watermelon, Pumpkin and Winter Squash 1.25 lb ai/A G1(3D)=Grass for hay, G2(3D)=Field corn, G2(7D) Brussel sprouts, cauliflower, collards, kale, kohlrabi G6(3D)=Mustards, G25(3D)=Cotton, G5(5D)=Watercress, G3(7D)=Rice, Sorghum, Wheat, Rye, Barley, Oats and Corn, G4(7D)=Blueberry( ULV), G5(7D)=Turnip, Broccoli, Apple, Sweet Corn, Beet, Horseradish, Parsnip, Radish, Rutabaga, Salsify, Sweet potato, G6(7D)= Cabbage and Cherry(ULV), G7(7D=Carrot, G8(7D)=Mango and Passion fruit, G9(7D)=Asparagus G10(7D)=Pears and Quince, G12(7D)=Guava and Papaya, G2(14D)=Alfalfa, Clover, Lupine, Vetch and Lespedenza 1.5 lbs ai/A **H2(7D)**=Celery, **H6(7D)**=Okra 1.56lbs ai/A I2(7D)=Potato, Sweet potato, I5(7D)=Onion, Garlic, Shallot, Leeks J6(5D)=Lettuce, J4(7D)=Blackberry, Raspberry, Loganberry, Boysenberry, Dewberry, 1.88 lb ai/A Currant, Gooseberry, **J3(7D)**=Cucumber, Chayote, **J6(7D)**= Strawberry, **J2(14D)**=Grapes K6(6D)=Strawberry(50% WP), K3(7D)= Spinach, Dandelion, Endive, Parsley and 2.03 lbs ai/A Swiss Chard, **K4(7D)**=Blackberry, Raspberry, Gooseberry, Loganberry, Dewberry, Currant and Boysenberry 2.50 lb ai/A L25(3D)=Cotton, L3(5D)=Figs, L3(7D)=Mustards, Walnuts, and Pecans, **L5(7D)**=Peas 3.43 lb ai/A M5(5D)=Tomato, Pepper, Eggplant N4(7D)=Apricots, N6(7D)=Cherry, 3.75 lb ai/A **N4(14D)**=Peach and Nectarine 4.7 lb ai/A O2(30D)=Avocado **P3(7D)**=Pineapple, **P4(7D)**=Chestnuts 5.0 lb ai/A 6.25 lb ai/A Q3(30D)=Oranges, Grapefruit, Lemon, Lime, Tangerine and Tangelo

#### **Tier II Assessment**

#### Summary

Since the EEC's derived from first-tier GENEEC simulations were above levels of concern (LOCs) for aquatic organisms, Tier II EEC's were calculated. The second tier assessment for malathion in surface waters utilized PRZM-EXAMS modeling and the review of available monitoring data. It is not possible to perform second tier modeling of malaoxon due to the lack of fate data on this toxic degradate. Required data for malaoxon include degradation (161-1), metabolism (162-1,4), and mobility (163-1,2) and well as data on solubility and rates of formation under suitable conditions.

PRZM 3.1 was used to simulate the agricultural field, and EXAMS 2.97.5 was used to simulate fate and transport in surface water. Each model scenario simulates a single site which represents the use of malathion on a particular crop. The weather and agricultural practices were simulated over multiple years, in this case 24 to 36, so the probability of an EEC occurring at that site can be estimated.

Five application scenarios were simulated, using crops which together represent more than 50% of malathion use in the United States as well as the highest use-rates proposed by the registrant. The EECs derived from these simulations were generally lower than those generated by Tier I GENEEC runs (see Table 10). Twenty-two additional crops have malathion application rates, numbers of applications and application intervals identical to one of the five crops simulated (see Table 1). The EECs generated from the five scenarios may be used as surrogates for these twenty-two crops, recognizing that these predicted EECs may vary due to geographical and other differences.

Monitoring and field studies were also examined in this second tier assessment. Studies reviewed include those associated with Mediterranean fruit fly and boll weevil eradication programs. Data from these studies (summarized in tables 10-13) shows in agricultural settings that the most important source of aquatic malathion is off-target drift and malaoxon is only detected at low concentrations. In urban areas, runoff is more important and malaoxon levels can be much higher.

## **PRZM-EXAMS Modeling**

PRZM-EXAMS estimates aquatic concentrations in a one hectare pond that is two meters deep next to a ten hectare plot. The pond receives both simulated drift and runoff from the field. PRZM models terrestrial pesticide fate and transport and EXAMS models the aquatic portion.

The Pesticide Root Zone Model (PRZM) is a one-dimensional, dynamic, compartmental model that can be used to simulate chemical movement in unsaturated soil systems within and immediately below the plant root zone. It has two major components-- hydrology (and hydraulics) and chemical transport. The hydrologic component for calculating runoff and erosion is based on the Soil Conservation Service curve number technique and the Universal Soil Loss Equation. Evapotranspiration is estimated either directly from pan evaporation data, or based on an empirical formula. Evapotranspiration is divided among evaporation from crop interception, evaporation from soil, and transpiration by the crop. Water movement is simulated by the use of generalized soil parameters, including field capacity, wilting point, and saturation water content.

Exposure Analysis Modeling System (EXAMS II) is a model that can receive progressive PRZM runoff concentration output to further predict aquatic pesticide concentrations in a simulated pond. The predicted concentrations over the period of time (usually 24-36 years) can be averaged over time to produce peak and time averaged concentrations which take into account aquatic degradation.

EFED has prepared standard PRZM input files for the five crops simulated. The locations used to build these scenarios were chosen to represent areas of greatest malathion use. EFED has prepared draft summary documents which describe the input parameters used to develop the standard scenarios. Once these documents have been finalized, they can be provided upon request.

The five input files were adapted to simulate the application of malathion for the respective crops and states represented in the standard scenarios. Chemical-specific input for malathion was derived to the greatest extent possible from the environmental fate database submitted to the EPA

by registrant Cheminova. Application rates, numbers of applications, and application intervals simulated were consistent with the maximum values requested by the registrants for establishing tolerances. Average application rates and numbers of applications were taken from BEAD Quantitative Use Analysis reports. Planting and harvest dates, and likely dates of malathion application, were chosen based on conversations with academic and extension crop specialists, or USDA references. Further details on crop and chemical specific inputs are presented in the appendices.

#### **Results**

The PRZM-EXAMS Tier II EECs for malathion are listed along with GENEEC Tier I EECs in the following table for comparison purposes.

**Table 10.** Summary of model results inputting maximal and typical use rates for crops with high malathion usage and high use rates. Intervals and the total number of applications used for these modeling runs were chosen to be conservative. By using maximum use rates (used in food residue tolerance limits), minimal intervals between applications, and the maximum number of applications the modeled use scenarios are expected to reflects a high exposure scenario.

PRZM-EXAMS results										
			Interval (days)	No. of applications	Model Comparisons					
Crop	% of total a.i.	Use rate (lbs a.i./A)			GEN	EEC	PRZM-EXAMS			
СТОР	applied / year¹	(100 011/11)	(uuj s)	иррисция	peak	56 d ave.	peak <sup>2</sup>	60 d ave. <sup>3</sup>		
		Max: 2.5	3	25	181	16.9	291	47.7		
Cotton	41.6%	Typ: 0.3	[3] <sup>4</sup>	4	20.6	1.95	7.9	0.50		
		Max: 1.25	7	3	56.1	5.24	26.7	1.95		
Sorghum	7.4%	Typ: 0.8	[7]	1	18.5	1.74	2.94	0.18		
		Max: 1.25	7	5	56.5	5.28	0.80	0.19		
Apple	2.14%	Typ: 0.7	[7]	3	31.4	2.93	0.59	0.09		
Citrus		Max: 6.25	30	3	226	21.2	156	10.7		
	0.49%	Typ <sup>5</sup> : 2.5	[30]	1	57.1	5.33	42.6	2.33		
		Max: 1.88	5	6	99.4	9.28	15.4	2.98		
Lettuce	0.45%	Typ: 2.0	[5]	1	45.7	4.26	5.63	0.56		

<sup>&</sup>lt;sup>1</sup>Pesticide data compiled by the National center for Food and Agricultural Policy for 1991-1993 and 1995.

## **Limitations of Modeling Analysis**

There are several factors which limit the accuracy and precision of this analysis including the selection of the high exposure scenarios, the quality of the input data, the ability of the models to represent the real world, and the number of years that were modeled.

Scenarios that are selected for use in Tier 2 EEC calculations are ones that are likely to produce large concentrations in the aquatic environment. It should represent a site that really exists and would be likely to have the pesticide in question applied to it. It should be extreme enough to provide conservative estimates of the EEC, but not so extreme that the model cannot properly simulate the fate and transport processes at the site. Currently, sites are chosen by best professional judgement to represent sites which generally produce EEC's larger than 90% of all site use for that crop. The EEC's in this analysis are accurate only to the extent that the site represents this hypothetical high exposure site. The most limiting part of the site selection is the use of the standard pond with no outlet. Obviously, a Mississippi pond, even with appropriately modified temperature data is not the most appropriate water body for use in all situations. Some water bodies would likely have higher concentrations. These would be shallow water bodies near agricultural fields that receive most of their water as runoff from agricultural fields.

The quality of the analysis is directly related to the quality of the input parameters. Most of the fate data for malathion is complete, however, there is little fate and transport data on toxic impurities and degradates such as malaoxon. In addition, the aquatic persistence inputs were derived from studies conducted under alkaline conditions which would be likely to increase degradation rates and reduce the conservatism of this analysis.

The models themselves represent a limitation on the analysis quality. While the models are some of the best environmental fate estimation tools available, they have significant limitations in their ability to represent some processes. Spray drift is estimated as a straight 5% of the application rate reaching the pond for each application from ground application. In actuality, this value should vary with each application from near zero to higher than 20%. A second major limitation of the models is the lack of validation at the field level for pesticide runoff. While several of the algorithms (volume of runoff water, eroded sediment mass) are well validated and well understood, no adequate validation has yet been made of PRZM 3.1 for the amount of pesticide transported in runoff events. Other limitations of the models used are the inability to handle

<sup>&</sup>lt;sup>2</sup>Peak concentration expected once in ten years.

<sup>&</sup>lt;sup>3</sup>The 60 day average value expected once in ten years.

<sup>&</sup>lt;sup>4</sup>Since data on typical intervals is not available the minimum interval was used in model runs with average use rates and number of applications.

<sup>&</sup>lt;sup>5</sup> Typical values for oranges.

within site variation (spatial variability), lack of crop growth algorithms, and an overly simple soil water transport algorithm (the "tipping bucket" method). Another limitation is that only thirty-six years of weather data was available for the analysis at most sites and less at others. Consequently, at best there is approximately 1 chance in 20 that the true 10% exceedence EEC's are larger than the maximum EEC in the calculated in the analysis. If the number of years of weather data could be increased it would increase the confidence that the estimated value for the 10% exceedence EEC was close to the true value.

There are certain limitations imposed when Tier II EEC's are used for drinking water exposure estimates. Obviously, a single 10 hectare field with a 1 hectare pond does not accurately reflect the dynamics in a watershed large enough to support a drinking water facility. A basin of this size would certainly not be planted completely to a single crop nor be completely treated with a particular pesticide. Additionally, treatment with the pesticide would likely occur over several days or weeks, rather than all on a single day. This would reduce the magnitude of the concentration peaks, but also make them broader, reducing the acute exposure but perhaps increasing the chronic exposure. The fact that the simulated pond has no outlet is also a limitation as water bodies in this size range would have at least some flow through (rivers) or turnover (reservoirs). Also, irrigation of crops in the desert scenarios was not considered in the models. EEC's would likely be higher if EFED had irrigation data available. In spite of these limitations, a Tier II EEC can provide a reasonable upper bound estimate of the concentration found in drinking water. Risk assessment using Tier II values can be used as refined screens to demonstrate that the risk is below the level of concern.

#### **Monitoring Data**

Monitoring data was collected through two USDA programs: the Boll Weevil Eradication Program and the Mediterranean fruitfly (medfly) control effort.

#### Agricultural

Agricultural runoff monitoring data and field studies are consistent with aerobic soil metabolism studies showing that malathion is normally rapidly degraded on soil to compounds of lower toxicity.

Malathion is water soluble and thus poses the potential to be dissolved in rain water and transported in runoff water from application sites if it not degraded. Levels of malathion in runoff water have been examined mostly using automatic runoff sampling equipment (ARSEs) which consist of collection bottles with funnels recessed in the ground at sites where runoff is expected. The amount of malathion in runoff is expected to be affected by numerous variables including the soil type, half-life on the particular soil, the amount of time between application and precipitation, the amount of precipitation, and vegetation. Table 11 shows runoff monitoring data from five treated cotton fields in the Boll Weevil program close to bodies of water. Sampling was performed close to the field (10-25 feet) and closer to the water (40-135 feet from the field). In most cases, malathion concentrations were lower when the interval between application and rainfall was longer and/or distance from the field was farther. These observations are expected

since increasing the interval allows for more degradation to occur and farther runoff travel distances allow malathion to penetrate soil and adsorb to soil particles before reaching shorelines.

Table 11. Field monitored runoff Cotton Bollweevil Control Program

Malathion levels were measured in runoff water from cotton fields after rain events. Two sets of measurements were made, one closer to the field and one farther from the field. Adapted from Environmental Monitoring Report: 1997 Southeast Boll Weevil Eradication Program Sensitive Sites and Environmental Monitoring Report: 1996 Southeast Boll Weevil Eradication Program.

	Field R	unoff	
field no. / sample distance from field	malathi	on conc (ppb)	time from application to rain
	closer to field	farther from field	(days)
1806-502 / near to field: 20'	9.3	1.9	1
farther from field: 110'	7.5	3.5	3
	>0.3	>0.3	6
1806-504 /	70	33	1
near to field: 20' farther from field: 40'	0.48	nd	6
2025-187 / near to field: 10' farther from field: 70'	0.42	0.53	2
2027-468 /	63	nd	1
near to field: 15' farther from field: 135'	nd	-	5
2100-200 / near to field: 25' farther from field: 50'	4.2	3.8	18
502 /	1.1	nd	3
near to field: 20' farther from field: 110'	0.5	nd	7
504 /	10.9	nd	1
near to field: 20' farther from field: 40'	41.8	15.6	3
	146	93.5	7
7806 /	0.9	0.5	?
near to field: 0' farther from field: 45'	1.7	1.1	6
	<0.3	0.3	14
325 / near to field: 15'	8.54	.82	2
farther from field: 60'	35.8	16.2	9

nd = none detected.

In monitoring projects the stability of malathion in still water has been examined. A half-acre pond surrounded by cotton fields with a 25 foot buffer was monitored for malathion (USDA BWEP 1993). Pesticide drift was determined to be the most important mechanism of contamination of the pond. Residues levels in the pond were lower before treatment (<0.1-0.44 ppb) and higher immediately after malathion application (<0.33-91.4 ppb). In most cases malathion in the pond degraded to <0.33 ppb within 7 days. Runoff was only a minor contributor of residue to the pond but only two rainfalls occurred during the sampling period. The malathion in the runoff samples collected were 9.75 and 76.3 ppb one day after the first and last treatments, respectively. Other natural bodies of water within treatment areas, but not intentionally receiving direct spray, showed no detectable levels of malathion 3-27 days after applications ceased (USDA BWEP 1995).

**Tables 12 a,b,c.** Spray drift to adjacent moving water. Malathion levels in moving water adjacent to cotton fields was measured before and after treatment. Measurements were made downstream from the field every 15 minutes from one hour before until 2-3.25 hours after application. Application was made when wind was not blowing directly over the water.

	S		pray Drift Veevil Eradicat				
site/comments	application (aerial /	treatment #	days since last treatment	time (	(min) / dow	nstream malathi	on (ppb)
3.00 00	ground)			before treatment	time	after treatment	time
McCall's Creek:	a	1	?	nd		nd	
The creek was separated from the field (13.3 acre) by a continuous 600-700' buffer of 30-60' trees.	a	2	8	nd		nd	
	a	3	6	nd		nd	
	a	4	7	nd		nd	
	a	5	7	16.1	-60	nd	
North River:	g	1	?	-		nd	
The field (8.3 acre) is separated	g	2	5	nd		nd	
from the river by a continuous buffer of mature hardwoods and	g	3	7	nd		nd	
moderately dense understory approximately 125' deep.	g	4	6	< 0.33	-45	< 0.33	45
	g	5	6	< 0.33	0	< 0.33	0-120
	a	6	10	1.54	-45	1.44	60
	a	7	6	< 0.33	0	< 0.33	0-120
	a	8	7	1.77	-60	1.46	0
	a	9	10	0.42	-45	0.55	45

Pursley Creek:	a	1	?	nd		3.54	135
The field (95.3 acre) was	a	2	7	nd		0.39	120
separated from the creek by 100' of mature hardwoods with a	a	3	7	nd		1.03	30
dense understory.	a	4	7	nd		< 0.33	75-120
	a	5	7	6.63	-30	3.80	120
	a	6	6	nd		3.35	150
Stewart Creek:	ου	1	?	<del>nd</del> nd		nd	
The field (19.2 acre) was separated from the creek by a 25'	00	2	8	<0.33	-60	nd	
buffer of low -lying kudzu vegetation.	a	3	7	nd		7.69	60
·	a	4	5	nd		3.16	75
	90	5	7	0.52		< 0.33	0-240
	g	6	4	0.51		10.89	15
	Ø	7	5	<0.33		<0.33	15, 105, 135- 250
	a	8	6	1.01		4.52	60
	a	9	12	< 0.33		3.49	105

b.)

Spray Drift Environmental Monitoring Report Boll Weevil Cooperative Eradication Program: 1995 Texas Lower Rio Grande Valley											
			downstream malathion (ppb) / time (min)								
site/comments	aerial/ ground	treatment #	before treatment	time	after treatment	time					
#204060311/	?	1	0.324	-15	0.297	15					
Canal 200' from treated field.	?	2	4.89	-15	7.26	30					
#2144070704 Canal 40' from treated	?	1	6.38	-30	11.4	0					
field	?	2	2.27	-45	1.87	0					
#212080704/ Canal 150' from treated	?	1	4.81	-45	4.15	30,120					
field	?	2	2.4	-30	4.37	120					
	?	3	5.92	-45	4.21	0					

Spray Drift Environmental Monitoring Report Southern Rolling Plains Boll Weevil Eradication Program - 1994-1995											
				peak downst	ream malathion (ppb	o) / time (min)					
site/comments	method of app.	treatment #	before treatment	time	after treatment	time					
Concho County stream (10303-	Hi-Boy	1	0.849	-15	6.95	105					
Samples collected 0.25 miles	Mist blower	2	0.695	-45	86.9	225					
downstream	Mist blower	3	0.273	-45	0.503	210					
Concho River	Mist blower	1	0.676	-15	0.813	0					
(10708-2707) Samples collected 0.25 miles	Mist blower	2	0.871	-60	0.589	150					
downstream	Mist blower	3	2.24	-60	7.45	15					

Wide buffer strips (125-700 feet) with high vegetation appeared to reduce malathion drift to sensitive areas to levels below detection while narrower and lower buffer afforded less protection (Table 12). With aerial applications, 8 of 19 applications lead to higher aquatic malathion concentrations, whereas only 1 of 10 ground applications resulted in higher malathion levels. Thus aerial applications appear more prone to drift than ground applications. Although increased malathion levels in the streams, rivers, and canals examined after nearby treatments decreased rapidly, decreases are likely due primarily to the movement of contaminated water downstream. To assess malathion stability in moving water a sampling station further downstream would be required along with measurements of the flow rate of the water.

#### Residential

Monitoring data suggests that urban malathion use poses the highest risk of contaminating surface water. However, use data is not available to correlate with monitoring data to determine which particular uses have the greatest impact. Total usage and use rates in specific cities is also unavailable. Targeted urban monitoring and preliminary fate experiments suggest however that malathion contacting anthropogenic surfaces is likely to convert to the oxon and has a high runoff potential.

Malathion concentrations in water in and around urban medfly treatment areas in California and Florida have been measured. Although risk assessment of malathion use for medfly control is not included in this document (these generally fall under section 18 local need uses) the monitoring studies associated with this use provide information on malathion fate and transport in residential settings. In urban areas not involved in medfly control measures malathion can be found in runoff water at higher levels than agricultural areas. A monitoring report by United States Geological Survey showed that higher residues are found in urban areas. In this analysis of 11 urban streams (604 samples) and 37 agricultural streams (1530 samples) malathion concentrations were higher in the urban tributaries.

It is likely that proposed residential uses will result in aquatic contamination. Residential malathion uses include outdoor home and garden, public park, and commercial use as well as residential mosquito control. Home use formulations may be applied as a "... spray to lower foundation of house, patios and garbage cans ... along fences; to firewood piles; and other infested areas." (Ortho Malathion 50 Plus Insect Spray label). Malathion on the surfaces described on the this label is likely to persist longer and be more available for runoff than malathion on soil. Fyfanon ULV formulation is applied at 0.2-0.23 lbs/A aerially at 150 mph over residential areas for mosquito control. In addition to covering anthropogenic surfaces it is likely that moderate sized bodies of water receive direct spray during normal aerial mosquito control use. In medfly treatments, malathion is mixed with a bait mixture and applied aerially at nearly the same rate as in mosquito control but with large buffers (up to 200 feet). Medfly applications in residential areas provide useful information on the fate and transport of malathion in these settings, but it is very likely that the smaller particles produced from the ULV formulation used in mosquito control results in more drift than the baited mixture for medfly. Thus, medfly monitoring data of drift will be expected to underestimate drift from ULV mosquito use.

In medfly control efforts larger bodies of water are "flagged" to avoid direct malathion treatment. Thus, contaminated water bodies presumably received insecticide residues by drift and runoff. On average reservoirs in the treatment area which were flagged to avoid direct spray contained 0.16 ppb before treatments and 2.59 ppb immediately after treatment (Table 12). All waters in and around the treatment area, whether protected or not, showed increased malathion levels immediately after treatment. In general, applications were performed approximately weekly with no noted aggregate accumulation of malathion in water.

Rainwater runoff in California medfly treatment area contributed greatly to malathion levels in a stream passing through the treatment area. After precipitation, inflow into the treatment area contained less than 1 ppb while downstream water contained up to 203 ppb malathion. Maxima in 1990 and 1981 were 44.1 and 583 ppb (Environmental Monitoring Results of the Mediterranean Fruit Fly Eradication Program, Riverside County 1994).

**Table 13 a Medfly spraying and malathion levels in bodies of water.** Malathion was measured immediately before and after spraying a bait formulation at ~0.17 lbs ai/A from a altitude of 300 feet. This data was adapted from A Characterization of Sequential Aerial Malathion Applications in the Santa Clara Valley of California, 1981.

Aq	quatic r	nalathio	1 concent	trations	in ppl	o resul	ting fr	om me	edfly ap	plica	tions	
	treat-	days		ma	alathion				mal	aoxon (p	opb)	
site	ment #	since last spray	no. of sample	before spray	S.d. Error	after spray	S.d. Error	no.of samp	before spray	S.d Err	after spray	S.d Err.
Unprotected <sup>1</sup>	1	*	14	*	*	4.94	2.71	*	*	*	*	*
waters	2	9	6-16	0.20	0.05	18.66	5.81	1	*	*	18.0	*
*	3	11	13-15	1.50	1.17	9.78	2.47	*	*	*	*	*
	4	7	14-15	0.48	0.13	95.4	53.2	1-2	0.64	*	1.9	0.20
	5	7	13-14	0.66	0.12	4.97	1.05	4-5	0.19	0.0 46	0.63	0.17
	6	7	11-12	0.57	0.20	23.4	11.6	1-4	0.90	*	0.35	0.10
Average	-	8.2	-	0.68	0.33	26.19	12.81					
Protected <sup>2</sup> natural	1	*	20	0.091	0.058	0.33	0.078	*	*	*	*	*
waters	2	9	20	0.12	0.07	0.56	0.10	*	*	*	*	*
	3	11	19-20	0.056	0.028	0.90	0.15	*	*	*	*	*
	4	7	14-15	0.12	0.07	1.25	0.22	*	*	*	*	*
	5	7	20-22	0.040	0.019	2.10	0.41	1	*	*	0.40	*
	6	7	15-19	0.053	0.040	0.39	0.089	2	*	*	0.45	0.25
Average	-	8.2	-	0.080	0.048	0.92	0.17					
Flagged reservoirs	2	9	2	0.18	0.03	0.75	0.65	1	*	*	2.7	*
reservoirs	3	11	2	*	*	0.50	0.10	*	*	*	*	*
	4	7	19-20	0.033	0.024	8.39	3.81	2	*	*	0.92	0.29
	5	7	10-12	0.51	0.30	1.90	0.94	*	*	*	*	*
	6	7	8	0.075	0.062	1.42	0.41	1	0.1	*	0.83	*
Average	-	8.2	-	0.16	0.083	2.59	1.18					
Reservoirs outside	2	9	2	0.05	0.05	0.34	0.07	*	*	*	*	*
treatment	3	11	2-4	0.10	0.10	1.0	0.55	*	*	*	*	*
area	4	7	10	0.03	0.03	0.30	0.16	*	*	*	*	*
	5	7	10	0.036	0.024	0.14	0.058	1	1.3	*	*	*
	6	7	8-10	0.18	0.074	0.21	0.087	*	*	*	*	*
Average	-	8.2	-	0.079	0.056	0.40	0.19					

**Table 13 b.** Malathion level in 29 ponds in Florida exposed to a.) direct or b.) indirect malathion spray in medfly control. Samples were collected within eighteen hours of approximately weekly treatments of 0.15 lbs/A. Unprotected bodies of water were ~0.1 miles in length and may have received runoff from surrounding watersheds. Protected waters were rivers or larger lakes. Statistically, values below the detection limit (0.1 ppb) were treated as 0 ppb and values below limit of quantitation (0.3 ppb) were treated as 0.15 ppb. The data was adapted from the Environmental Monitoring Report: Cooperative Medfly Project Florida, 1997.

a.)

		Unprot	ected aquatio	sites		
-:4-		before			after	
site	no. of samples	ave (ppb)	stdev (ppb)	no. of samples	ave (ppb)	stdev (ppb)
Fairgrounds	8	0.06	0.07	9	1.20	1.54
Palm river	9	0.78	0.72	7	3.97	3.24
Ragen Park	6	14.12	14.17	7	35.75	27.50
University Square Mall	7	0.04	0.07	7	3.77	3.67
Pond Lake	6	4.11	4.35	10	9.25	11.78
Bloomingdale Area	9	0.81	0.71	9	6.12	7.22
Carrolwood	7	1.05	2.01	6	4.77	3.75
Town and Country	6	1.10	1.15	5	6.88	3.07
McDill Site	5	0.12	0.06	4	5.20	2.33
Brandon Town Center	5	3.50	1.86	8	65.71	149.18
Lowry Zoo	7	0.14	0.22	6	1.55	1.86
Sun 'n Fun	8	0.09	0.07	10	7.28	15.48
Hamilton Creek	6	0.61	0.41	7	10.74	19.51
Fagle Lake	7	1.60	2.29	7	13.99	10 39

<sup>&</sup>lt;sup>1</sup>Unflagged and within the treatment area.

<sup>&</sup>lt;sup>2</sup>Flagged to avoid treatment or outside the treatment area.

<sup>\*</sup> No data.

		Protec	ted aquatic si	tes			
-:		before		after			
site	<u>n</u>	ave (ppb)	<u>s.d.</u> (ppb)	<u>n</u>	ave (ppb)	<u>s.d.</u> (ppb)	
Moore's lake	10	0.36	0.78	10	0.76	1.66	
Lake Weeks	12	0.69	0.67	11	4.85	4.08	
Lake Valrico	12	0.03	0.06	11	2.84	6.71	
Lake Kathy	12	0.43	0.91	11	5.91	9.15	
Lake Walden	6	0.21	0.14	6	2.21	2.37	
Alafia River	6	0.13	0.17	6	1.93	4.06	
Hillsborough River	8	0.35	0.39	8	5.02	9.13	
Platt Lake	2	0.08	0.08	2	0.85	0.15	
Lake Magdalene	2	0.08	0.08	2	0.80	0.20	
Lake Carroll	2	0.31	0.16	2	1.65	0.55	
Crystal Lake	9	0.02	0.05	9	0.46	0.74	
Lake Horney	10	0.03	0.06	9	3.47	3.86	
Banana Lake	7	0.21	0.33	7	2.48	3.97	
Crews Lake	7	0.23	0.19	7	0.82	0.96	

Residential settings are expected to be composed of numerous surfaces which may be physically and biologically impervious to malathion. The relative quantities and effects of adsorption and degradation on concrete, roofing, metal, and plastics is unknown in the residential settings where malathion may be sprayed for medfly and mosquito control. Monitoring results suggest that the residential surfaces increase availability of malathion for runoff probably due to lack of microbial activity which decreases metabolism, less water content which decreases hydrolysis, and little adsorption. Although the application rate for mosquito control is low relative to agricultural use (0.20-0.23 lbs/A for aerial mosquito control versus 0.18-6.25 lbs/A for agricultural pest control), application over wide areas may be concentrated in storm drain systems along with malathion from home garden and commercial site use.

The concentration factor appears to be greater in residential settings when comparing residential and agricultural runoff. This is consistent with the results of several USGS and USDA monitoring studies. Preliminary monitoring results for malathion in surface water (USGS 1997) show malathion was detected above 0.01 ppb with a 2.61% frequency in agricultural streams while in urban streams the frequency was 20.86%. The USDA monitoring studies for boll weevil control show an average runoff concentration of 15.5 ppb (Table 11) while average downstream creek concentrations in the urban Santa Clara Valley of central California were 177 ppb during 1981 malathion spraying for medfly.

The highest levels of aquatic malaoxon found in a search of available data was a result of medfly control efforts in California (CDFG 1982). The following table is derived from the monitoring study during the malathion spraying in the Santa Clara Valley. Samples were taken 2-3.5 hours

after the first rainfall 6 days after the last application. These runoff concentrations are much higher than agricultural runoff levels.

**Table 14.** Malathion and malaoxon concentrations in creeks after malathion applications in the Santa Clara Valley.

Sampling Loc	eation	malathion	(ppb)	malao	xon (ppb)
		average	sd	average	sd
Adobe Creek	50' upstream	449	17.7	164	33.2
	drain	583	40.3	328	18.4
	100' downstream			169	-
Stevens Creek	50' upstream	159	-	68.0	-
	drain		73.5	147	4.2
	150' downstream	156	23.3	68.0	-
Guadalupe Creek, site 1	50' upstream	1.9	0.2	0.8	0.3
	drain	142	-	147	4.2
	150' downstream	23.5	2.1	22.0	-
Guadalupe Creek, site 2	50' upstream	137	25.4	212	9.2
	drain		12.0	250	8.5
	150' downstream	169	6.4	231	8.5

Fate data for malathion clearly show that its major routes of degradation are through aerobic microbial metabolism and hydrolysis. Both of these routes are expected to be lower on inert, dry surfaces; thus malathion persistence would be expected to be increased. Malathion persistence on steel plates is extended relative to soil with only 15% lost in two days (State of California 1996) compared to several soils on which 50% can be degraded in 8 hours. Slowed malathion hydrolysis and metabolism is likely to result in increased malaoxon levels via abiotic oxidation. On the steel plate study mentioned previously, malaoxon accounted for 5% of the degradates, significantly higher than the maximum of 1.8% on soil reported by the registrant.

#### **Limitations of Monitoring Analysis**

Although a relatively large amount of monitoring data is available for malathion, the level of detail among the studies varies. Malathion is used on more than 60 crops and settings but detailed monitoring studies were conducted mostly in conjunction with medfly and boll weevil eradication measures. Other studies lack important data such as detection limits, surroundings, wind

direction, and rainfall data making comparisons between studies difficult. Though boll weevil eradication data may be considered to reflect malathion behavior on crops grown in the same geographical areas, more data is necessary to improve quality and to allow detailed statistical analysis. Malathion applications and monitoring associated with medfly control mostly occur in residential settings and thus are probably also representative of residential mosquito control in urban areas.

#### 3. Ground Water Assessment

Malathion has some mobility characteristics similar to other chemicals that have been detected in ground water. In addition, malathion has been occasionally detected in ground water at levels ranging from 0.03 to 6.17 ppb.

USGS data in the National Water Quality Assessment show a malathion detection in ground water at > 0.05 ppb. The EPA Pesticides in Ground Water Data Base 1971-1991, National Summary reports malathion detections in ground water in California (1 detection out of 499 wells sampled at a concentration of 0.32 ppb), Mississippi (2 detection out of 263 wells, concentrations of 0.03-0.053 ppb) and Virginia (22 detections made in 9 of 138 wells samples with a range of concentrations of 0.007-6.17 ppb). All malathion detections in Virginia ground water were made in Westmoreland county as part of the Watershed/Water Quality Monitoring for Evaluating BMP Effectiveness program. Westmoreland is a coastal county and is approximately equally comprised of agricultural and forested land. Analytical detections in this study were conducted using gas chromatography with an electron capture detector and confirmed with flame photometric detector. Samuel Johnson of Westmoreland County Extension provided information on malathion use in this county. In recent years most of the agricultural malathion usage was for the control of cereal leaf beetle on barley and wheat. However, since 1995 a synthetic pyrethroid has replaced most malathion usage in Westmoreland. Mosquito abatement is not a major use of malathion in Westmoreland.

EFED believes these monitoring data illustrate that malathion has the potential for movement into groundwater, especially on soils with low organic matter and high sand content.

Cheminova disputes the ground-water data reported in the PGWDB. In particular, it calls into question the analytical methods used to generate the data in the Virginia study. In addition, Cheminova indicates that the maximum detection in the study was 3.12 ppb, not 6.17 ppb. Noting Cheminova's doubts for the Virginia data, EFED suggests a ground-water concentration estimate of 3.1 ppb for malathion for human-health risk assessment. This value is more conservative than SCI-GROW modeling results using maximal parameters for use on cotton (0.142 ppb). Since this monitoring result is specific for malathion EFED assumes the concentration of malaoxon will not exceed the concentration of malathion. Thus, EFED suggests conservative ground water concentration estimates of 3.1 ppb for malathion and 3.1 ppb for malaoxon.

The fact that malathion is detected in ground water means that under certain conditions it persists longer than its reported 1 to 3 day half lives emphasizing the need for further studies defining degradation rates under unfavorable conditions.

# 3. Ecological Effects Hazard Assessment

### **Mode of Action Summary**

Several reviews of malathion and organophosphate toxicology exist including Matsumura (1985).

Malathion's mode of action is through acetylcholinesterase (AChE) inhibition which disrupts nervous system function. AChE is a enzyme made of protein which cleaves the neurotransmitter acetylcholine in nervous system junctions. Inhibiting this enzyme leads to accumulation of the neurotransmitter thus causing signals in the nervous system to persist longer than normal. Typical symptoms for pesticides which act in this manner are defecation, urination, lacrimation, muscular twitching and weakness, and halted respiration. Malathion, along with other phosphorodithioate insecticides (those containing two sulfur atoms bonded to phosphorus) must be oxidized before they have inhibitory potency and toxicity. Oxidation occurs via cytochrome p450 and results in the conversion of the P=S group in malathion to P=O forming its oxon, malaoxon (Murphy et al., 1968). This alteration of the phosphate group enables the molecule to covalently bind AChE resulting in long lasting inhibition of the enzyme.

Malaoxon binds to AChE by mimicking the structure of enzyme's natural substrate, acetylcholine. The similarity between the size, shape, and properties of malaoxon and the neurotransmitter allow it to "fit" in the acetylcholine binding site on the enzyme. Altering the structure of malaoxon or malathion reduces the ability of the oxon to bind AChE resulting in detoxification of the molecule. Detoxification reactions may be a result of enzyme or chemical action on the molecule. Detoxification occurs very rapidly in mammals giving pure malathion a very low acute toxicity [LD50 in rats is 12,500 mg/kg (Fukuto 1983)]. Common detoxification reactions for malathion (and malaoxon) are ester hydrolysis, demethylation, and phosphorothiolate ester hydrolysis. When one or more of these detoxification steps are blocked by another chemical the toxicity of malathion is increased and the added chemical is considered to synergize malathion toxicity. Chemicals which increase the rate of malathion's conversion to malaoxon may also be synergists.

Important detoxification steps occur through nonspecific esterase enzymes which are capable of cleaving malathion to less toxic degradates. Biological and environmental degradates of malathion with greatly lowered toxicity include malathion  $\alpha$ ,  $\beta$ , and diacids, and O-desmethyl malathion (Matsumura 1985). Since organophosphate insecticides are inhibitors of esterases (most specifically AChE) they possess the ability to block detoxification enzymes. Several organophosphate impurities present in technical malathion are known to synergize malathion toxicity probably through blocking malathion detoxification. The toxicity of several malathion impurities alone is also very high (eg the LD50 of O,O,S-trimethyl phosphorothioate in rats is 15 mg/kg, or 833 times more toxic than pure malathion) and cause delayed toxicity suggesting a

mode of action other than AChE inhibition. Impurities can be produced through improper storage of malathion as evidenced by a 35% increase in the acute toxicity of technical malathion stored at 40°C for 6 months (Fukuto 1983).

### **Toxicity to Terrestrial Animals**

### 1. Birds, Acute and Subacute

An acute avian oral toxicity study using the technical grade of the active ingredient (TGAI) is required to establish the toxicity of pesticides to birds. The preferred test species is either mallard duck (a waterfowl) or bobwhite quail (an upland gamebird). Results of avian oral acute tests with Malathion are tabulated below.

**Table 15. Avian Acute Oral Toxicity** 

Species	%ai	LD50(mg/Kg) (CL's)	Toxicity Category	MRID	Author	Classi- fication 1
Mallard duck	95	14D LD <sub>50</sub> =1485 (1020-2150)	Slightly toxic	00160000	Hudson, R.H. and Tucker, 1984, USFWS	Core
Ring-necked pheasant	95	14D LD <sub>50</sub> =167 (120-231)	Moderate	00160000	Hudson R.H. and Tucker, 1984, USFWS	Supple- mental
Horned lark	95	14D LD <sub>50</sub> =403 (247-658)	Moderate	00160000	Hudson, R.H. and Tucker, 1984, USFWS	Supple- mental
Sharp tailed grouse	tech	LD50 =220 (171-240)	Moderate	Reference	Crabtree, D.G., 1965, Denver Wildlife Res. Center, USFWS	Supple- mental

<sup>1</sup> Core (study satisfies guideline). Supplemental (study is scientifically sound, but does not satisfy guideline)

Based on the data reviewed to date malathion displays low to moderate acute oral toxicity to the 3 species of birds tested by USFWS laboratories. Another referenced study was mentioned in the 1966 McEwen and Brown field study with Sharp tailed grouse (see field study section of this document). The study was conducted at the USFWS Denver Wildlife Research Center and is considered valid supplemental data. McEwen and Brown observed a similar LD50 with wild caught grouse. The most sensitive species tested was the ring-necked pheasant. The acute oral data does fulfill 71-1 testing guidelines.

Two subacute dietary studies using the TGAI are required to establish the toxicity of a pesticide to birds. The preferred test species are mallard duck and bobwhite quail. Results of subacute dietary tests with malathion conducted by USFWS laboratories are tabulated in table 16 below.

**Table 16. Avian Subacute Dietary Toxicity** 

Species	%ai	LC50(ppm)	Toxicity Category	MRID	Author	Classi- fication
Ring-necked pheasant	95	8D LC <sub>50</sub> =2639 (2220-3098)	Slightly toxic	00022923	Hill, E.F. et al USFWS, 1975	Core
Bobwhite quail	95	8D LC <sub>50</sub> =3497 (2959-4011)	Slightly toxic	00022923	Hill, E.F. et al USFWS, 1975	Core
Japanese quail	95	8D LC <sub>50</sub> =2962 (2453-3656)	Slightly toxic	00022923	Hill, E.F. et al USFWS, 1975	Supple- mental
Mallard duck	95	8D LC <sub>50</sub> >5000	Nearly non-toxic	00022923	Hill,E.F. et al USFWS, 1975	Core

Based on the test results reviewed to date malathion displays low toxicity to 4 avian species on a subacute dietary basis. These studies were not submitted or funded by the registrant, but were conducted at the Patuxent Wildlife Research Center by U.S. Fish and Wildlife Service researchers. These studies are considered acceptable by the Agency and fulfill 71-2 guideline requirements.

#### 2. Birds, Chronic

Avian reproduction studies using the TGAI are required for malathion because the following conditions are met: (1) birds may be subject to repeated or continuous exposure to the pesticide, especially preceding or during the breeding season, and (2) information derived from mammalian reproduction studies indicates reproduction in terrestrial vertebrates may be adversely affected by the anticipated use of the product. The preferred test species are mallard duck and bobwhite quail. Results of these tests are tabulated below.

**Table 17. Avian Reproductive Sensitivity** 

Species	%ai	LOEL Effected Parameters	NOEL	MRID	Author	Classi- fication
Bobwhite quail	96.4	21WK LOEL=350 ppm -regressed ovaries and reduced egghatch At 1200 ppm- reduced shell thickness, # eggs layed, egg viability	110 ppm	43501501	Beavers, J. Wildlife Intl.,1995	Core
Mallard duck	94.0	20WK LOEL =2400 ppm Growth and viability	1200 ppm	42782101	Biolife Assoc. 1993	Core

The guideline (71-4) is fulfilled by the studies above. Chronic exposure to malathion in diets produced moderate toxicity to terrestrial avian species and low toxicity to waterfowl species

tested to date. At food exposure concentrations of 350 ppm 4 of 15 female bobwhite quail exposed to malathion for 21 weeks displayed regressed ovaries and abnormally enlarged/flaccid gizzards. The same observation was made in females at the 1200 ppm level. A reduction in numbers of eggs hatched from eggs set was observed at 350 ppm. Reduced egg production, viability of eggs, and embryo survival as well as an increase in the number of cracked eggs (a possible indication of the weakening of the shell structure) was observed at 1200 ppm. Effects to adults at 1200 ppb included weight loss, reduced feed consumption, some mortality, and clinical signs of toxicity

### Non Guideline Studies Or Field Observations with Avian Species

Over it's long history a great amount of field testing or specialized laboratory testing has been conducted with Malathion products by agricultural research laboratories, universities, registrants, and government research laboratories. A number of these studies dealing with non target avian species and contained in Agency files are briefly summarized below. This is not a complete compilation of all available data on malathion, as a literature search for this chemical could involve thousands of citations conducted during a 30-40 year period of use.

### Teratological and Embryonic Effects

In a University of Ottawa study 0.1 ml of solution injected into leghorn chicken eggs proved lethal to 50% of the embryos after 7 days (dependent on age). 4-5 day old embryos were most susceptible. Abnormalities included lack of feathers, smaller size, beak, plumage and hind limb defects.(Greenburg, J. and. N. Latham, 1968). In other studies where malathion was injected into eggs at 50 mg/egg chicks showed shortening of legs and bleaching of feathers (Marliac and Mutchler, 1963). For hen eggs injected with 25, 100, 200, 300, 400, and 500 ppm of malathion dissolved in acetone hatchability was significantly reduced at higher levels with hatches of 85%, 87%, 62%, 71%, 42%, and 6%, respectively (Dunachie and Fletcher, 1969). A number of studies were conducted where malathion or malaoxon were injected into chick embryos (Walker, 1971 and Khera and Lyon, 1968). Malaoxon caused reduced survival of embryos at a concentration of 30 micromoles, and those that did survive had severe abnormalities. Malathion at 15 micromoles produced less severe abnormalities.

Starlings fed 160 ppm of malathion for 12 weeks showed 30% decrease in AChE and 50% decrease in 1 acetate dehydrogenase activity (Dieter, Michael P., 1975 )

In a Montana study 52 live trapped sharptailed grouse were given oral doses of dieldrin, malathion, and lactose (controls) and released after tagging. They were subsequently observed by capture or radio tracking. The lethal dose of malathion was observed to occur between 200-240 mg/kg. Reaction to malathion occurred within 72 hours - either death or full recovery. Sublethal signs included depression, slow reactions, blinking, head nodding, and eventual heart or respiratory failure. Radio tracked grouse displayed normal to severe reactions once released. 8 of 12 birds were recovered. Predators are suspected in the disappearance of unrecovered birds (in one case a bird moderately dosed with dieldrin was confirmed killed by a coyote). Grouse that were dosed carried transmitters up to 12 days after release. All confirmed predator kills had

received what were considered sublethal doses of the test material. Other birds were discovered to have been attacked and injured. The radio transmitters did not hinder all birds as many were recovered in healthy condition. The sublethal effect of the malathion and dieldrin on survivability are suspected. All controls survived and successfully bred. (McEwen, Lowell and Robert L. Brown, 1966. MRID 113233)

In an Indian Agricultural Research Institute study, house sparrows, *Passer domesticus* were offered treated grain with 5% ai malathion dust. At a concentration 56.7g/56.8 kg of grain (or approximately 100 ppm) to determine deterrent effect. The sparrows showed 75% reduction in feeding on treated seed vs. untreated seed (4 grams of treated seed consumed vs 21 gms. of untreated seed on average). Orally dosed birds showed increased respiration, head droop, ejection of white fluid from mouth, chronic and tonic convulsions at 5 mg/kg or more. Birds that did recover did so in about 1 hour. AChE inhibition was 83%, 75%, 50% and 25% at 19 mg, 5 mg, 2 mg and 1 mg per kg of body weight, respectively within 5 minutes of ingestion. The 1 and 2 mg/Kg dosed birds recovered in 24 hours. 57% and 18% mortality was observed at 10 and 5 mg/kg feed residue concentrations. (Mehrotra, K. N. et al, 1966.)

In aerial application of malathion was made over Winnipeg in July 1983 malathion was applied as ULV solution using 95% malathion. Application rate was 210 ml/ha over the entire city to control mosquitos. 41 sparrows and 39 pigeons were collected within 2 weeks of spraying. Caged exposed sparrows were sacrificed and examined as well. Slight, but not statistically significant, differences were noted (6-12% variation) in AChE levels of post spray--to prespray birds. Some reservation is expressed that study birds may all have been exposed to ground fogging applications prior to aerial application exposure.(Kucera, Emil. Manitoba Dept. of Environment and Workplace Safety and Health, 1987).

An experimental program to control melon flies on the Island of Bota in the Northern Marianas Islands, provided the USFWS with an opportunity to monitor avian populations while subjected to exposure to malathion laced bait sprays (Cue-lure) that were aerially applied. Applications were made at 3 week intervals beginning in Oct. 1988 at up to 5 -30 gms/hectare depending on bait type. Of the 10 native species counted 5 increased in number and 5 decreased. The author was not certain if this was a normal annual fluctuation or one caused by pesticides. Populations of the white throated ground dove, the Phillipine turtle dove, and possibly the bridled white eye were significantly lower in the following year. No acute mortality was reported. The other 20 native species were observed and populations appeared unaffected. Even insectivorous species did not appear to suffer population decreases. (John Engbring, U.S. Fish and Wildlife Service, Honolulu, Hawaii, 1989).

During 1964-1968 bollweevil control programs on cotton game and nongame bird populations near cotton fields were observed. Applications were aerial at 12 to 16 oz. (approx. 1.2 lb ai) of technical malathion per acre, with up to 7 applications made at 5-22 day intervals. No major differences in weight gain were noted between treated and control birds. No toxicant related mortality was noted after 3 applications of malathion. No dead birds were located adjacent to

fields. However, sublethal indicators other than weight were not measured. (Parsons, Jack K. and Billy Don Davis, Texas Parks and Wildlife Dept., 1971).

### Field Observations of Effects to Multiple Groups of Terrestrial Organisms

In "The Ecology of a Small Forested Watershed Treated with the Insecticide Malathion S<sup>35</sup>." (S.Giles, Robert H., Jr., 1970), Aerial Application to 2 adjoining Ohio watersheds was observed with one treated and the other untreated. Malathion was radio tagged with Sulfur 35 radio nuclide. Two 20 acre watersheds (primarily deciduous forests) were selected for comparison. Application rate was 2 lbs/acre and 4 applications were made. Spray residue cards were placed under application areas for residue analysis. Residue collection discs were also suspended above the canopy using helium filled balloons. Glass discs were placed in the trees as well as the shrubs and in soil/litter surfaces. Radioactivity was high in the tissues of plants sampled in the treated areas indicating active systemic uptake of malathion. New shoots and leaves showed especially high levels of radioactivity. Metabolites of malathion showed up in new stem and leaf growth up to one year after application.

Though no adverse effects to bacterial or fungal populations were observed, fungi had higher concentrations of radioactivity than surrounding plant tissues. Soil micro arthropods were briefly affected. In experimental cans containing soil and earthworms, more dead earthworms were found in the treated plots (not statistically significant numbers) and several had radioactivity within their tissues suggesting uptake of the radio labeled malathion. Birds showed some reaction up to 48 hours post application, but no lasting effects noted. Lack of singing was observed throughout treated areas immediately after application and persisted for 2 days. By day 4 singing intensity was equal in treated and control areas. Possible explanations include sublethal insecticidal response, behavioral response due to loss of food, or possibly temporary emigration from the treated areas. Some radioactivity was detected in collected bird's whole organ tissues. Insectivorous birds had the highest detection of radioactivity on feathers. For observed small mammal populations effects were mixed. Up to a 45% reduction in population of white footed mice Peromyscus leucopus novaboracensis was estimated for the treated areas, based on pre and post treatment trapping counts. However, no difference in populations of short-tailed shrews or black-tailed shrews was determined, though residues were detected in costal cartilage, kidney, and heart tissues samples. Chipmunk populations were reduced 55% in treated areas following applications. The study author concludes "As with the mice this is not a lethal effect, but apparently one of productivity and survival." Larger mammals appeared unaffected. As might be expected, insect numbers (all observed species) were greatly reduced. However, populations recovered quickly. In stream nets located at temporary dams dead insect numbers were 1270 1 hour after spraying and decreased to 640 and 598 individuals collected 2 and 3 hours after spraying, respectively.

A number of field observations were recorded following 9 ULV aerial applications of malathion over Hale County by C123 cargo planes for mosquito control. AChE levels were determined in the sparrows prior to spraying and 30 hrs. following applications 1, 3, 5 and 7. Only 9.5% of the banded sparrows (11 of 116) were recaptured. No bird carcasses were recovered. Brain AChE levels in the captured sparrows were not significantly inhibited - but a slight reduction from 0.023

to 0.018 was observed. Unprotected honeybees were killed, but covered hives were not seriously effected. (Elwood F. et al., 1971).

## Mammals, Acute and Chronic Toxicity

Wild mammal acute toxicity testing is required on a case-by-case basis, depending on the results of lower tier laboratory mammalian studies, intended use pattern and pertinent environmental fate characteristics. In most cases, rat or mouse acute toxicity values are obtained from the Agency's Health Effects Division (HED) and substitute for wild mammal testing. These toxicity values are reported below.

Table 18. Mammalian Acute Oral and Chronic Dietary Toxicity

Specie	%ai	LD50 (mg/Kg)	Study ID	NOEL (parameter)	Study ID and Author	Cate- gory
Mice	Tech 90%	720-886	Doc #000389	500 ppm ( growth -2 yr. chronic study)	Reference Doc#000389 N.C.I.,1979	N.R.
Guinea pig	Tech	570	Doc # 000389	Not determined	Reference Doc#000389 Pham.Exp.Ther. 12:327,1953	N.R.
Sheep	Tech	<150	Doc # 000389	Not determined	Reference Doc# 000389 J.Vet.Am.Medical Ass., 1957	N.R.
Cow	95%	560(adult ) 80 (calf)	Doc # 000389	Not determined	Ref Doc # 000389 Golz and Shaffer, 1956	
Cat	Tech	>500	Doc # 000389	Not determined	Reference Doc# 000389	N.R.
Rat (Wista r albino)	57% EL	1763	Doc # 000317	ataxia, tremors, salivation, diarrhea observed	Reference Doc#000317 Doc# 000389	Suppl.
Rat	Tech	390-2100	Doc # 000389 Am. Cyanamid 1956	1000 ppm (growth) 32 day ChE reduction at 100 ppm 240 mg/kg/day reduced pup survival and BW	Reference Doc#000389 Karlow and Martin, 1965	N.R.

Rabbit	Tech	>900	Doc# 000389, J. Econ. Entomol. 48:139	50 mg/kg/day resorption of embryos	MRID 260123 Ref.Doc.#000389 Food and Drug Research Lab,1984	N.R
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In one rat study oral LD50 ranged from 1000 to 1845 mg/Kg with females being more sensitive than males.

The results of mammalian laboratory indicate that malathion is slightly toxic to mammals on an acute oral basis. Sublethal effects may occur at concentrations as low as 100 mg/Kg for certain species. Reproductive effects are not expected unless concentration remain at 500-1000 mg/Kg for extended periods of time.

#### **Other Studies with Mammals**

In white rats alteration of EEG (elevated excitability of nervous system) at 75 and 438 mg/kg, and reduced acetocholinesterase levels were observed. The test rats exposed to malathion showed a reduced ability to run a maze with increased numbers of errors.(Desi, I. et al 1976).

Rats treated with malathion via oral ingestion began excreting the radio labeled malathion in their urine within 2 hours after ingestion. By 24 hours 83.4% of the radio labeled material was excreted in the urine (Bourke, J.B. et al New York State Agricultural Experiment Station, Cornell University, 1968).

In the 1970 study by R.H. Giles (see previous summary) certain species of small mammals (white-footed mice and chipmunks) showed significant population reductions(30-55%) after treatment of a forest area with 2 lb ai/A of malathion. Larger mammals and interestingly, shrews which are often sensitive due to high metabolisms, were not observed to have been effected. Population reductions were not observed to be related to acute adult mortality, but rather to reduced reproductive success or possibly effects on survival of young

## **Effects To Reptiles**

The Agency has not reviewed extensive laboratory toxicity data pertaining to In general, the Agency uses avian toxicity thresholds in the determination of hazard to reptiles. However, in one reported study oral ingestion of organophosphate pesticides and the resulting percent mortality was measured for Carolina anoles. For malathion the acute LD50 was determined to be 2324 mg/Kg (Hall R.J. and D.R. Clark, 1982). Mitchell and Yutema (1973) observed abnormal development in of embryos of the common snapping turtle exposed to malathion.

### **Non-target Beneficial Insect Toxicity**

#### **Terrestrial Insects**

A honey bee acute contact study using the TGAI is required for malathion insecticide products because uses will result in honey bee exposure. A honey bee foliar residue contact toxicity study is required using the typical end-use product because many uses will result in potentially adverse honey bee exposure to vegetative surfaces after application. Results are tabulated below.

Table 19. Nontarget Pollinator Insect Acute and Foliar Contact Toxicity

Species	%ai	LD50 (ug ai/Bee)	Toxicity Category	MRID	Author/ year	Classificatio n
Honey bee	57EC	8 HR Foliar Contact LD <sub>50</sub> <1.6	Highly toxic	41208001 41284701	1989	Core
Honey bee	Tech	48 HR LD <sub>50</sub> =0.20	Highly toxic	05001991	1978	Core
Honey bee	Tech	96 HR LD <sub>50</sub> =0.709	Highly toxic	0001999	1967	Core
Honey bee	Tech	N.R. LD <sub>50</sub> = 0.27 (0.22-0.29)	Highly toxic	05004151	1968	Core
Honey bee	Tech	48 HR LD <sub>50</sub> =0.38	Highly toxic	05004003	1968	Core

The results indicate that malathion is highly toxic to bees on an acute contact basis either through exposure to direct spray or through foliar residue contact within 8 hours after spray is applied. The guidelines 141-1 and 141-2 are fulfilled by these studies.

#### **Toxicity to Terrestrial Insects with Aquatic Lifestages**

Though not required, a number malathion studies on toxicity to aquatic insect larvae conducted by the U.S. Fish and Wildlife Service laboratories were reviewed. These studies, conducted under static acute aquatic invertebrate testing protocols, are indicative of possible effects to species of insects which spend the early stages of their lives as aquatic larvae. The larvae are sometimes a food source for certain predatory species of aquatic organisms. Many of the adults of these species may later form important links in the food chain for insectivorous birds, mammals, fish, amphibians and reptiles as well as predatory aquatic and terrestrial invertebrates. Elimination of these taxa during developmental stages could conceivably impact adult population levels of these insects.

Table 20. Toxicity to Aquatic Larvae of Terrestrial Insects

Species % ai	LC <sub>50</sub> (C.L.s) in PPB	Toxicity	MRID	Author/Year	Classifi- cation
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Stonefly Claasenia sabulosa	95%	LC50=2.8 (1.4-4.3)	Very high	40098001	Mayer and Ellersieck, USFWS, 1984	Supple- mental
Stonefly, Pteronarcella badia	95%	LC <sub>50</sub> =1.1 (0.78-1.5)	Very high	40098001	Mayer and Ellersieck, USFWS, 1984	Supple- mental
Stonefly, Isoperla sp.	95%	LC <sub>50</sub> =0.69 (0.2-2.4)	Very high	40098001	Mayer and Ellersieck, USFWS, 1984	Supple- mental
Damselfly, Lestes congener	95%	LC <sub>50</sub> =10 (6.5-15.0)	Very high	40098001	Mayer and Ellersieck, USFWS, 1984	Supple- mental
Caddisfly, <i>Hydropsyche</i> sp.	95%	LC <sub>50</sub> =5.0 (2.9-8.6)	Very high	40098001	Mayer and Ellersieck, USFWS, 1984	Supple- mental
Caddisfly, <i>Limnephalus</i> sp.	95%	LC <sub>50</sub> =1.3 (0.77-2.0)	Very high	40098001	Mayer and Ellersieck, USFWS, 1984	Supple- mental
Snipefly, Atherix variegata	95%	LC <sub>50</sub> =385 (245-602)	High	40098001	Mayer and Ellersieck, USFWS, 1984	Supple- mental

Based on the data reviewed to date for aquatic early life stages of terrestrial non-target insects malathion is classified as highly to very highly toxic to aquatic larvae of these species.

### Field Observations of Effects to Non-Target Insects

Over it's long history a great amount of field testing has been conducted with Malathion products in field test situations by agricultural research laboratories, registrants, and government research laboratories. A number of these studies dealing with non target insects are briefly summarized below.

During a six week period - baited sprays were applied with large droplet sizes (200-300 *mu* mean diameter). Malathion and malaoxon were detected in water throughout monitoring period. Rain runoff to storm drains produced concentrations up to 583 ppb in existing streams. Since bait sprays did not attract honeybees it was believed that they would be unaffected. However, nontargeted lacewings and dipterids were attracted (mainly scavenger flies) to the bait and killed.(Oshima, R. S. 1982; California Medfly Report)

Significant Impact on Honeybees was observed in a study conducted near San Francisco using to Mediterranean Fruit Fly Malathion Bait Sprays. Significant mortality was observed during 48 hours post-application. Cause was determined to be pesticide contaminated pollen (2.06 ppm (mean)) and body residue levels of 0.9 -5.3 ppm. Data from Stockton study also showed increased mortality which was partially attributable to nearby application of Sevin, (alfalfa fields), Kabbate and sulfur dust (tomato fields). Reduced flight activity was observed at both exposed sites after pesticide applications. Other mortality may have occurred in the fields that was not measurable. (Gary, Norman E. and Eric C., Mussen, Dept. of Entomology, Univ. of California, Davis 1984).

In a University of California study, protein hydrolysate bait spray and malathion applications were monitored and effects to nontarget beneficial insect predators common in urban trees were measured. Drop cloths were placed under trees and dead fallen insects were collected and identified. 17 species of aphids, numerous dipterids, butterfly (lepidoptera) larvae, spiders, cynipoidea, and hemiptera appeared to be heavily effected. Also pscoptera were reduced. (Dahlsten, Donald L., University of California, 1983).

In studies with two species of stonefly naiads 96 hour acute exposures under static conditions included malathion exposure. Even when the naiads were removed after displaying sublethal effects (convulsions or tremors) and placed in clean water, they generally died within 24 hours (Jensen, Loren D. and Anden R. Gaufin, Dept. Zoology, University of Utah, 1964.(MRID 00065497)).

In a Washington University study six colonies of honeybees were placed in a 125 acre alfalfa field 36 hours before aerial application. 2 hives were covered with wet burlap during application and burlap was removed 24 and 48 hours post application. Two hives were left uncovered in the sprayed fields. 2 other colonies were placed 2.25 miles from the application site and one of these was covered with burlap for 48 hours. 8 fluid oz of malathion ULV concentrate was applied per acre by aerial spray at 50 feet altitude in a 125 foot swath on Aug 14. Package bee cages (150-200 bees) were also placed in fields 2 and 7 hours after application for a 3 hour exposure period. Caged bees were also exposed to foliar residue samples at intervals following the application. Bee mortality was higher than normal for 4 days after application. Those covered with wet burlap suffered the highest mortality 1 day after the covers were removed. Bees caged on treated foliage also exhibited higher than normal mortality. Check (control) colonies showed between 500 and 838 dead bees at hive entrances. Treated hive mortalities ranged from 1298 ((unprotected) to 2582 (entrance covered) honeybees. Bees which contacted treated foliage showed from 100% (2 hours-1 day post application) mortality to 14% mortality (4 day old residues) versus an average of 5% mortality for control bees. Malathion residues on foliage ranged from 28.8 ppm at application to 0.4 ppm 14 days after application. Residues remained over 25 ppm for 4 days following application after which a rainfall event occurred. Grasshopper populations were greatly reduced from 12/sq. yd. to less than 1/sq yd. three days after treatment. Lygus bugs were also controlled for up to 3 weeks. Interestingly, the target organisms, Alfalfa weevils and larvae, were not totally controlled. Lady beetles populations were reduced for up to 3 weeks following applications. (Johansen, C.A. et al. Washington State University College of Agriculture. 1965).

### **Terrestrial Wildlife Field Incidents**

The Agency reviews and records all wildlife mortality incidents reported independently or under 6a2 provisions of FIFRA regarding use of pesticides or pesticide mixtures. These incidents are reported to the Agency by a variety of sources including registrants, private organizations and local, state, or federal agencies. A summary of all terrestrial incidents reviewed by the Agency following use of malathion products or mixtures is provided in table 21 below.

Table 21

<b>Location and Date</b>	Incident	Description	Probability
Oregon, 1/1/85	I000130	5000 acres of alfalfa treated with malathion by USDA- extensive mortality of honeybees collecting nectar from blossoms reported	Probable
Florida, 1997 Medfly Program, Hillsborough County area	USDA Medfly Incident Report	Three incidents involving mortality of ducks were reported along with over 40 fish kills that were investigated. All occurred where malathion bait formulations were used near ponds.  6/22-10 to 14 Ducks killed-Seminole Htsbaits used  6/14-Duck kill-NW Hillsborough sector-baits used  6/25-Duck kill-Rodrie pond-baits applied aerially	Possible- but unlikely. Only routes believed to offer logical exposure route- oral ingestion of baits or dermal exposure- residue concentration too low to =LD50.

The incidents where duck mortality was reported in Florida medfly program investigations were determined to be more likely caused by some other toxicant. Though fish kills did occur in the ponds, actual residues were well under those which would be expected to cause oral toxicity in mallard duck(1485 mg/Kg). In the case of the June 14 fish kill an oily substance was observed on the moribund ducks. Park service personnel had also sprayed herbicides near the pond (Glyphosate and Copper). Maximum malathion concentration on vegetation was only 3.0 ppm far below avian toxicity thresholds. The Agency would tend to agree with USDA that malathion was not the primary cause of death in the duck kill incidents.

### **Acute Toxicity to Fish**

Two freshwater fish acute toxicity studies using the TGAI are required to establish the toxicity of a pesticide to freshwater fish. The preferred test species are rainbow trout (a coldwater fish) and bluegill sunfish (a warmwater fish). Acute toxicity testing with estuarine/marine fish species using the TGAI is required for malathion because the end-use product is intended for direct application to the marine/estuarine environment and the active ingredient is expected to reach this environment because of its use near estuarine environments. The preferred estuarine test species is sheepshead minnow. A selection of numerous(over 50) tests considered valid and reviewed by EPA are summarized below.

Table 22. Freshwater(FW) and Marine/Estuarine(SW) Fish Acute Toxicity

Species Tested	% ai	LC50 and CLs in PPB	Toxicity	MRID	Author	Classi- ficatio n
Freshwater Fish Spe	cies					
Bluegill sunfish(FW)	95	96 Hr LC <sub>50</sub> =20 (16-25)	Very High	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Bluegill sunfish(FW)	95	96 Hr LC <sub>50</sub> =30 (10-88)	Very High	40098001	Mayer and Ellersieck, USFWS, 1984	Core

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Redear sunfish(FW)	95	95 Hr LC <sub>50</sub> =62 (58-67)	Very high	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Rainbow trout(FW)	95	96 Hr LC <sub>50</sub> =4 (2-7)	Very high	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Yellow perch(FW)	95	96 Hr LC <sub>50</sub> =263 (205-338)	High	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Largemouth bass(FW)	95	96 Hr LC <sub>50</sub> =250 (229-310)	High	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Carp(FW)	95	96 Hr LC <sub>50</sub> =6590 (4920-8820)	Moderate	40098001	Mayer and Ellersieck, USFWS, 1984	Supl.
Fathead minnow(FW)	95	96 Hr LC <sub>50</sub> =8650 (6450-11500)	Moderate	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Channel catfish(FW)	95	96 Hr LC <sub>50</sub> =7620 (5820-9970)	Moderate	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Coho salmon(FW)	95	96 Hr LC <sub>50</sub> 170 (160-180)	High	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Cutthroat trout(FW)	95	96 Hr LC <sub>50</sub> =174 (112-269)	High	40098001	Mayer and Ellersieck, USFWS 1984	Core
Brown trout(FW)	95	96 Hr LC <sub>50</sub> =101 (84-115)	High	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Lake trout(FW)	95	96 Hr LC <sub>50</sub> =76 (47-123)	High	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Black bullhead catfish(FW)	95	96 Hr LC <sub>50</sub> =11700 (9600-14100)	Moderate	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Green sunfish(FW)	95	96 Hr LC <sub>50</sub> =1460 (900-2340)	Moderate	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Walleye(FW)	95	96 Hr LC <sub>50</sub> =64 (59-70)	Very high	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Tilapia(FW)	95	96 Hr LC <sub>50</sub> =2000 (N.R.)	Moderate	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Goldfish(FW)	95	96 Hr LC <sub>50</sub> =10700 (8340-13800)	Moderate	40098001	Mayer and Ellersieck, USFWS, 1984	Core
Estuarine Marine	Fish	Species				
Spot(SW)	95	Flowthrough 48 Hr LC <sub>50</sub> =320(N.R.)	High	40228401	F. L. Mayer, USEPA	Supl.
Striped mullet(SW)	95	Flowthrough 48 Hr LC <sub>50</sub> =330(N.R.)	High	40228401	F. L. Mayer, USEPA	Supl.

Longnose killifish(SW)	95	Flowthrough 48 Hr LC <sub>50</sub> =150(N.R.)	High	40228401	F.L. Mayer, USEPA	Supl.
Sheepshead minnow(SW)	95	Flowthrough 96 HR LC <sub>50</sub> =33.0 (14-63)	Very high	41174301	Bowman, J 1989, ABC Laboratories	Core
Striped bass(SW)	95	96 Hr LC <sub>50</sub> =60(N.R.)	Very high	156311	Wellborn, T. 1971 Reference	Supl.
Sheepshead minnow(SW)	57 EC	96 HR LC <sub>50</sub> 55	Very high	41252101	Bowman,J. ABC Labs, 1989	Core

Based on the extensive data reviewed for malathion toxicity to freshwater and estuarine/marine fish the pesticide is classified as very highly to moderately toxic to fish dependent on the sensitivity of the tested species. In many cases these studies were done with static test systems, no measured concentrations, and varying pH levels which can influence the actual toxicity or calculation of toxicity values for a chemical with fate characteristics such as malathion. This is due to the hydrolytic instability of the compound. Thus, actual mean concentrations which caused the mortality may have been much lower after 96 hours of exposure than is indicated. This would have influenced the calculation of LC50 levels if they had been based on measured concentrations instead of nominal 0 hour concentrations. The 72-1 and 72-3 guidelines for acute toxicity testing of fish are fulfilled by the data reviewed above.

### **Chronic Toxicity To Freshwater and Estuarine Fish**

A freshwater fish early life-stage test and/or an estuarine fish early life stage test using the TGAI is required for malathion because some end-use products may be applied directly to water and other product uses are expected to contribute residues which may be transported to water from the various intended use sites. In addition the following chronic testing guideline conditions are met: the pesticide is intended for use such that its presence in water is likely to be recurrent, aquatic acute LC50 are less than 1 mg/l, the EECs in water are equal to or greater than 0.01 of any acute LC50, studies of other organisms indicate the reproductive physiology of fish may be affected. The preferred test species are the rainbow trout and the sheepshead minnow.

A freshwater fish full life-cycle test using the TGAI is required for malathion because the end-use product is intended to be applied directly to water and is expected to be transported to water from the intended use sites. In addition, the following conditions were met: the EEC is equal to or greater than one-tenth of the NOEL in the fish early life-stage or invertebrate life-cycle test, and studies of other organisms indicate the reproductive physiology of fish may be affected. The preferred test species is fathead minnow. A satisfactory full life cycle test has not been submitted, though a pilot lifecycle study with fathead minnow has been attempted. Results of this test are tabulated below.

An estuarine/marine fish early life stage or life-cycle test using the TGAI is required for malathion due to the application of malathion for mosquito and medfly control near estuarine habitats and use on crops associated with areas near these habitats. This study may be waived if further modeling results indicate that EEC levels in estuaries will not exceed the early life stage NOEC levels for a freshwater species, or if the registrant does not continue to support these uses. The preferred test species is sheepshead minnow.

Table 23. Freshwater and Marine Fish Chronic Toxicity Test Results

Species	Guide- line	%ai	LOEC in PPB	NOEC	MRID	Author	Cate- gory
Rainbow trout	72-4	94	97 day LOEC= 44	2 1 PPB	41422401	Cohle P., ABC Laboratories 1989	Core
Flagfish, Jordanella floridae	72-4	tech	110 day LOEC=11	8.6 PPB	Reference	Hermanutz,R., 1978*	Supple- mental
Fathead minnow	72-5	tech	158 day LOEC=350	N.D.	D234663	ABC Laboratories, 1997	Supple- mental

The guideline (72-4) is fulfilled for freshwater fish.

The guideline (72-4) is **not** fulfilled for a marine/estuarine fish species.

The guideline (72-5) is **not** fulfilled. Study aborted early due to malathion degradation problems.

### Non Guideline Aquatic Toxicity Studies with Fish

Interestingly, Hoff and Westman (1965) studied various combinations of malathion and dibrom to determine kill ratio for fish eradication efforts. A 3pt/2pt ratio of dibrom and malathion was reported to be an effective combination for use as a piscicide.

For malathion the squawfish estimated  $LC_{50}$  was 9.14 ppm (8.3 - 10) and the Bonytail chub  $LC_{50}$  was estimated as 15.3 ppm(14.4 - 16.4) based on nominal concentrations(Beyers, P. et al, 1993). Both of these species are endangered.

**Reviewers note:** The LC50 levels may have been lower if measured concentrations had been made and used in LC50 calculations. The second Beyers test also mentions an LOEC of 24.7 PPB for flagfish, *Jordanella floridae* in a previous 30 day exposure for survival/growth.

In a study examining malathion toxicity to killifish after spraying near a saltmarsh marsh in Odessa, Delaware, Darsie and Coraiden (1958) of the Delaware Agricultural Research Station used 381 wildcaught killifish (*Fundulus ocellaris*) 25 fish were placed in each of several metal

<sup>\*</sup> Hermanutz, R. 1978. Endrin and Malathion toxicity to Flagfish (*Jordanella floridae*). <u>Arch. Of</u> Environmental Contaminants and Toxicology 7:159-168

tubs containing 7 gallons of natural marshwater. An aerial spray was applied at 0.51 lb ai/acre of malathion mixed with 2 qts of diesel oil. Monitored rate was 167 droplets/inch². After 4 hours 26.3% of the fish died, 42.4% showed sublethal effects and 31.2% appeared unaffected. 26% of the sublethally effected fish died later even though placed in clean water while 74% recovered.

The study report also mentions field observation of extensive mortality to species of killifish during medfly spraying in Florida in 1958. (Applic.Rate was 0.2 - 0.75 lbs ai/A)

Acute toxicity study results reported in Quarterly Report - USFWS Research Laboratory, Columbia, Mo. 1967 were as follows, 1.3 gm Walleye  $LC_{50} = 62$  ppb Raw water, 0.9 gm Largemouth bass  $LC_{50} = 80$  ppb raw water, 1.4 gm - Bluegill  $LC_{50} = 110$  ppb raw water, bluegill  $LC_{50} = 130$  ppb in pond water and *Gammarus faciatus*  $LC_{50} = 0.8$  ppb

### **Species Sensitivity**

S.Giles (1970) demonstrated that effects on fish may be extremely species sensitive. Stream samples taken after aerial application to an Ohio forest showed no significant effects to mudminnows or blacknose dace. However, effects to brook sticklebacks were extensive with over 95% mortality in the treated area.

### Acetylcholinesterase inhibition in Fish

Acetylcholinesterase inhibition is reported in federally endangered Colorado Squawfish exposed to Carbaryl and Malathion (Beyers, P. & P.Sikoski, 1993). Squawfish were exposed for 32 days in flowthrough systems for the study of early life stage effects to this listed species. AChE inhibition was based on 24 hour exposure. Reduced AChE activity NOEC=371 ug/L and the LOEC=707 ug/l for malathion.. Beyers, P. (1993) also reported acetylcholinesterase inhibition in federally endangered Bonytail chub exposed to Carbaryl and Malathion withthe NOEC for acetocholinesterase inhibition and reduced growth in the Bonytail chub was 990 ug/L. Threshold conc. = 521 ppb

Brook trout, rainbow trout and coho salmon were subjected to stamina flow tunnel tests after exposure to 55% EC formulation of malathion at 40 - 300 ppb concentrations for 7-10 days. This type of test was used to imitate upstream migration. Coho salmon was the most sensitive species with AChE levels reduced 75%. The exposed fish were unable to perform 2/3 of work activity (swimming in current) as the unexposed fish (Post, George and Robert Leasure, Colorado State Chronic effects on atlantic spot, *Leiostomus xanthurus* (an estuarine species) University, 1974). were tested by Holland and Lowe, (Gulfbreeze Biological Laboratory, 1966). Test fish exposed to constant concentration of 10 ppb of malathion for 26 weeks showed a 30% reduction in brain AChE levels over levels in untreated fish. However, no other adverse effects on the spot were noted. After 1 week AChE levels returned to normal. At higher concentrations brain acetylcholinesterase inhibition in fish from malathion was more extensive. In another Gulfbreeze study pinfish (also an estuarine species) were wildcaught, acclimated for 3 weeks, and subjected to a flowthrough exposure for 72 hours at up to 500 ppb of malathion dissolved in acetone. Results indicated that malaoxon may the active AChE Inhibitor since the parent was not present 2 wks later. Inhibition of over 70% generally indicates impending death. This occurred at about 58

ppb. At 25 ppb AChE inhibition of about 34% observed, but with eventual recovery of the test fish (Coppage, et al., 1975).

Coppage and Duke (1971) studied the effects of several pesticides including malathion in estuaries along the Gulf of Mexico. AChE inhibition measurements were made in spot, croaker and mullet in Louisiana after spraying malathion for mosquito control. Collected fish were frozen and shipped on ice to Gulfbreeze. Normal levels were measured and reported to range from 1.08 to 1.45 before spraying commenced. After spraying AChE levels were reduced to as low as 0.09. Range of inhibition was measured at 97% to 11% inhibition. Inhibition in spot ranged from 97% to 11% inhibition. Inhibition in spot lasted over 1 week (still 36% inhibition). Second spray was made 18 days after first and mullet were killed while spot and croaker suffered further reduction in AChE. Inhibition may remain over one month after spraying.

### **Developmental and Behavioral Effects**

Chronic toxicity of malathion to the bluegill (*Lepomis macrochirus*) was demonstrated in studies conducted at EPA's Environmental Research Laboratory in Duluth, Minnesota (Eaton, John G., 1970). Fish were wild caught from local ponds and exposed at varying concentrations for over 8 weeks. Triton surfactant was added as solvent for stock solutions. Spinal deformation was observed at exposure level of <10 ppb with an estimated MATC >3.6 <7.4 ppb A reproductive NOEC was estimated to be 20 ppb based on reduced survival and numbers of eggs produced/female. All fish died at 80 and 40 ppb (within 16 days at 80 ppb and within 54 days at 40 ppb).

Abnormal locomotion associated with skeletal malformations in sheepshead minnow, *Cyprinodon variegatus*, was observed after embryos were exposed at 3 and 10 ppm with 25 eggs/concentration. Exposure appeared to produce skeletal malformations which impeded swimming ability of fry. NOEC was 1 ppm. 25% and 41% of the larvae were effected at 3 and 10 ppm, respectively. Delayed hatch was observed in the 10 ppm test group. (Weis, Peddrick and Judith Weiss, Rutgers University and New York Ocean Science Laboratory, Montauk, New York, 1975).

Woodward reported an observed loss of avoidance response in goldfish after 72 hr exposure to malathion at 1 and 5 ppm. (Woodward, Dan F., Sport Fisheries Research USFWS publication 77, 1969). Johnson tested the effects of five organophosphorous insecticides on thermal tolerance, orientation and survival of *Gambusia affinis*. Malathion effected the ability to survive thermal change with an  $EC_{50} < 100$  ppb. Mortality of 100% occurred at 500 ppb malathion for this species (Johnson, C.R. 1977).

Possible field implications from the types of effects to fish mentioned above might include reduced ability to capture prey, avoid predators, spawn or migrate successfully upstream

Chronic toxicity study results reported in Quarterly Report - USFWS Research Laboratory, Columbia, Mo. 1967 were as follows: 1/4 acre ponds containing bluegill and catfish and were

used to measure chronic effects when applications reached 0.002 and 0.020 ppm. No clear indication of significant growth or hematocrit count differences were seen.

Survival of juvenile sheepshead minnows, *Cyprinodon variegatus* was significantly effected for adults exposed to 9 and 18 ppb levels of malathion for 140 days. The NOEC was estimated at 4 ppb for this study. (Parrish, P.R. 1977, EPA-600/3-77-059).

### **Toxicity of Malathion Formulations to Fish**

A single study submitted by the registrant in 1989 with sheepshead minnow exposed to 57% EC formulation showed this product to be highly toxic with an LC50 of 33 ppb (MRID 41252101).

Chinook Salmon Fingerlings were exposed for 96 hours to concentrations of Malathion 500 at up to 240 ppb. Resulting LC<sub>50</sub> levels were 170 ppb after only 24 hours and 120 ppb after 96 hrs. 95% mortality occurred after 24 hours at 240 ppb. (Parkhurst, Zell and Harlan Johnson. USFWS, 1955 (Progressive Fish Culturist)).

### The Toxicity of the Hydrolysis and Breakdown Products of Malathion to Fish

Fathead minnow were statically exposed for 96 hours and also for 14 day under flowthrough conditions. Results demonstrated that diethyl fumarate was more toxic than the parent to this species and that synergistic effects occur between the parent and the two major degradates. Toxicity values for 4 confirmed and 9 proposed degradates to fathead minnow are provided. Diethyl fumarate  $LC_{50} = 4.5$  mg/L. For comparison the LC50 for malathion parent to fathead minnow from Mayer and Ellersieck's publication is 8.65 mg/L. (Bender, Michael E., University of Michigan, 1969).

Table 26. Toxicity of confirmed and proposed malathion degradates to fathead minnow.

<u>Degradate</u>	96 hour TLM in mg/L
Dimethylphosphorodithioic acid	23.5
Diethyl fumarate	4.5
2-mercaptodiethyl succinate	35.0
Dimethylphosphorothionic acid	42.5
Maleic acid	5.0
Diethyl maleate	18.0
Dimethyl phosphate	18.0
Dimethyl phosphite	225.0
Thioglycolic acid	30.0
Diethyl succinate	140.0
Diethyl dl-tartarate	650.0
Bis(hydroxymethyl) phosphinic acid	29.0
Ethylene phosphite	34.0

In later studies Bender examined the toxicity of malathion and its hydrolysis products to the eastern mudminnow *Umbra pygmaea* (Bender, Michael E., Virginia Institute of Marine Science, 1976).

Wildcaught fish were exposed for 96 hour using static systems and for 14 days using flow through systems. 10 fish exposed/concentration were exposed to five concentrations used dechlorinated tapwater as dilution water in 5 gallon tanks. For this species 2 mecapto diethyl succinate was shown to be most toxic of 4 degradates tested ( $LC_{50} = 0.32$  ppm). Diethyl fumarate  $LC_{50} = 1.47$  ppm (was least toxic).

### **Uptake and Retention of Malathion in Fish Tissues**

Bender (1969) used *Cyprinus carpio* as test species. Fish were exposed for 4 days at 2.5 ppm. Liver, flesh, blood, gills and brain were areas of highest concentration (in that order). Cook and Moore (1976) attempted to determine tissue concentrations of parent and metabolites in fish, oyster, and shrimp tissues. Pinfish were exposed to 75 ppb for 24 hours. Greatest tissue concentrations were the MCA and DCA metabolites. Malaoxon and parent malathion were not detected.

### **Toxicity of Malathion to Amphibian Lifestages**

Though extensive literature has not been reviewed for toxicity of malathion to adult or larval life stages of amphibians, there are data to suggest that malathion may have teratogenic effects to early life stages of some frog species if environmental concentrations exceed 1 ppm. In studies with developing frog embryos of the frog, Microhyla ornata, gross abnormalities in skeletal development were noted for tadpoles which had been exposed for several days to malathion formulated spray (50% EC) concentrations ranging from 1 to 20 ppm. Control embryos hatched in 48 hours and were actively swimming at the end of 96 hours with no observed abnormalities. In treated embryos abnormalities observed included spinal curvature, blister development, and abnormal swimming behavior at concentrations ranging from 5-10 ppm. At 1 ppm only some behavioral abnormalities were observed including twitching of tails or swimming in circles. At concentrations >10 ppm malathion was highly embryo-toxic.(Pawar, K..R., Dept. Of Zoology, University of Poona, India, Bulletin of Environmental Contamination Toxicology, 31:170-176(1983). Mayer and Ellersieck have listed the acute toxicity of malathion to tadpoles of Fowlers toad, *Bufo woodhousei*, and the chorus frog, *Pseudacris triseriata* to be 420 ppb and 200 ppb, respectively. Powers, et al (1989) found that the LC50 for Bufo woodhousei exposed for 4-5 weeks was 200 ppb. These acute values are considered highly toxic.

In "The Ecology of a Small Forested Watershed Treated with the Insecticide Malathion S<sup>35</sup>."(1970), Giles reported that toads adsorbed high loads of residues into tissues. However the route of intake of residues was not certain (skin adsorption, ingestion, etc)

E. A. Rosenbaum studied the effects of malathion exposure to developing embryos of the South American toad *Bufo arenarum*. At exposure levels ranging up to 30 mg/L embryonic development appeared normal. However, at the 44 mg/L a 67% mortality was observed after 5 days exposure. An 8% mortality was observed in the control embryos. At this test level

additional signs of abnormal development included downward curvature of the spine, tail lashing, body twisting, pigmentation loss, and appearance of hydropecic vessicles. A significant inhibition of acetylcholinesterase, butyrylcholinesterase, and aliesterase activity was evidenced for the entire five day exposure period. No significant differences in levels of phospholipid, organic phosphate, or inorganic phosphate were detected between controls and the 44 mg/L test group (Rosenbaum et al, 1988).

In earlier studies with both dieldrin and malathion de Llamas (1985) also examined the effects of exposure of amphibians during early developmental stages. Malathion was administered at 0.0047, 0.47 and 47.3 mg/L test levels using dilutions of a 94.6% technical grade of malathion with 0.5% ethanol as a solvent. After 5 days of exposure a 100% mortality of fertilized embryos occurred at 47.3 mg/l, but larval development proceeded to completion at the lower test concentrations. All test concentrations reduced acetocholinesterase activity from 45% to 90% during the 23 day monitoring period (measurements made at 4, 7, 14, and 23 days).

# **Acute Toxicity to Freshwater and Marine/Estuarine Invertebrates**

A freshwater aquatic invertebrate toxicity test using the TGAI is required to establish the toxicity of a pesticide to aquatic invertebrates. The preferred test species is *Daphnia magna*.

Acute toxicity testing with estuarine/marine invertebrates using the TGAI is required for malathion because the end-use product is intended for direct application to the marine/estuarine environment or the active ingredient is expected to reach this environment because of its use near estuarine habitats. The preferred test species are mysid and eastern oyster. Results of freshwater and estuarine invertebrate acute toxicity tests reviewed by the Agency are tabulated below.

Table 24. Freshwater and Marine /Estuarine Invertebrate Acute Toxicity

Species Tested FW=Freshwater SW=Marine species	% ai	EC50 or LC50 in PPB	Toxicit y	MRID	Author	Classi- fication
Freshwater Inverte	brate :	Species				
Water flea, <i>Daphnia</i> pulex(FW)	95	48 Hr EC <sub>50</sub> =1.8 (1.4-2.4)	Very high	40098001	Mayer and Ellersieck, USFWS, 1986	Core
Scud, Gammarus lacustris(FW)	tech	48 Hr LC <sub>50</sub> =1.8 (1.3-2.4)	Very high	05009242	FWS Laboratories, 1969	Core
Scud, Gammarus fasciatus(FW)	95	96 Hr. LC <sub>50</sub> =0.5 (N.R.)	Very high	40098001	Mayer and Ellersieck, USFWS, 1986	Core
Daphnid Simocephalus serrulatus(FW)	95	48 Hr LC <sub>50</sub> =0.69 (0.44-0.79)	Very high	40098001	Mayer and Ellersieck, USFWS, 1986	Supple- mental

	1				I	
Crayfish, Orconectes nais (FW)	95	96 Hr LC <sub>50</sub> =180 (140-230)	High	40098001	Mayer and Ellersieck, USFWS, 1986	Supple- mental
Glass shrimp, Palaemonetes kadiakensis(FW)	95	96 Hr LC <sub>50</sub> =12 (N.R.)	High	40098001	Mayer and Ellersieck, USFWS, 1986	Supple- mental
Seed Shrimp,  Cypridopsis  vidua(FW)	95	49 Hr LC <sub>50</sub> =47 (32-69)	High	40098001	Mayer and Ellersieck, USFWS, 1986	Core
Water flea, Daphnia magna(FW)	57E C	48 Hr EC <sub>50</sub> =2.2 (1.9-2.5)	High	410297-01	Burgess, D. ABC Labs, 1989	Core
Water flea, Daphnia magna(FW)	95	48 Hr EC <sub>50</sub> =1.0 (0.7-1.4)	High	40098001	Mayer and Ellersieck, USFWS, 1986	Core
Sowbug, Asellus brevicaudus(FW)	95	96 Hr LC <sub>50</sub> =3000 (1500-8500)	Modera te	40098001	Mayer and Ellersieck, USFWS, 1986	Supple- mental
Estuarine Marine S	pecies	}				
Mysid, <i>Mysidopsis</i> bahia(SW)	94	96 Hr LC <sub>50</sub> =2.2 (1.5-2.6)	very high	41474501	Forbis, A., ABC Lab.,1990	Core
Pink shrimp, Penaeus duorarum(SW)	95	48 Hr LC <sub>50</sub> =280 (N.R.)	High	40228401	F.L. Mayer, USEPA, 1986	Supple- mental
Eastern oyster,  Crassostrea virginica (SW)	95	96 Hr LC <sub>50</sub> >1000	Not con- clusive	40228401	F.L. Mayer, USEPA, 1986	Supple- mental
Eastern oyster, Crassostrea virginica(SW)	57% EC	96 Hr EC <sub>50</sub> =2960 (N.R.)	Modera te	42249901	Wade, B and J. Wisk, ESE, Inc. 1992	Core
Blue Crab, Callinectes sapidus(SW)	95	48 Hr LC <sub>50</sub> >1000	Not con- clusive	40228401	F.L. Mayer, USEPA, 1986	Supple- mental

Since the LC50/EC50 values are in the range of 0.5 to 3000 PPB, malathion is classified as very highly to moderately toxic to aquatic invertebrates on an acute basis, dependent on the sensitivity of the tested species. Many of the studies above were conducted under static conditions with no measurement of actual residue levels. Thus, actual  $LC_{50}$  values might have been even lower than those reported if they had been based on measured concentrations (expected to be lower due to degradation). The guidelines 72-2 and 72-3 for invertebrate acute testing are fulfilled by these studies.

### **Chronic Toxicity to Freshwater and Marine Invertebrates**

Freshwater and estuarine/marine aquatic invertebrate life-cycle tests using the TGAI is required for malathion since the end-use product may be applied directly to water or is expected to be transported to water from the intended use site, and the following conditions are met: (1) the

pesticide is intended for use such that its presence in water is likely to be continuous or recurrent regardless of toxicity, (2) aquatic acute LC50 or EC50 are less than 1 mg/l, and (3) the EEC in water is equal to or greater than 0.01 of any acute EC50 or LC50 value. In addition, testing with other organisms indicate the reproductive physiology of invertebrates may be affected. The preferred test species are *Daphnia magna* for freshwater and *Mysidopsis bahia* for estuarine marine scenarios. Results of these tests are tabulated below.

Table 25. Freshwater and Marine/Estuarine Aquatic Invertebrate Life-Cycle Toxicity

Species	%ai	LOEC (parameter)	NOEC	MRID	Author	Classifi- cation
Water flea(FW)	94	21D LOEC= 0.10 PPB	0.06 PPB	41718401	Blakemore,G and D.Burgess, 1990	Core
Mysid(SW)		No Data				Required

The guideline (72-4) is fulfilled for freshwater species.

The guideline (72-4) is **not** fulfilled for estuarine species. A full life cycle study for mysid or other acceptable marine/estuarine species is required for the proposed uses of malathion.

### Effects on Development, Survival, and Other Activities of Aquatic Invertebrates

In a study designed to investigate effects to larvae development of crabs Bookhout and Costlow (1976) exposed mudcrabs, *Rhithropanopeusn horrisii* and blue crabs, *Callinectes sapidus* to malathion, mirex, and methoxychlor. In the case of malathion mudcrab larval survival was significantly reduced (12% to 100%) at 11 to 20 ppb, respectively. They did not survive past 2nd local stage at 50 ppb. Development time was also delayed between stages. Blue crab larvae development was slightly delayed but significant reduction in survival to megalopa stage was seen at concentrations of 50 ppb and less significantly reduced at 20 ppb. Total mortality in all stages was high in concentrations of 20 ppb or above compared to acetone controls.

Desi, et al (1976) tested the effects of malathion exposure to laboratory rats, freshwater mussels, daphnia and guppies. Adductor muscle activity was measured in the freshwater mussel *Anodonta cygnea*. Freshwater mussel larvae (glochiddia) shell closing activity was measured for 30 larvae over 3 min period after exposure to concentrations ranging between 100 and 100,000 ppb of malathion. *Anodonta cygnea* showed significantly reduced activity during 48 hour exposure at 10,000 ppb. No change noted at 1000 ppb or less. Glochiduim were less active at 1 ppb but showed similar activity as the controls at 0.1 ppb (NOEL). Guppies exposed to 100, 1000, 10,000, 10,000 and 100,000 ppb of malathion. were killed at 1000 ppb or above. The LC<sub>50</sub> for guppies was calculated to be 819 ppb. For the 30 daphnia were exposed to 100,000, 10,000, 1000,100, 10 and 1 ppb, in 300 ml of water (test repeated 3 times)100% mortality was observed at 10 ppb or above. No effects were observed at 1 ppb.

Despite the effects observed in mussels by Desi, Keller (1995) did not observe high acute toxicity of malathion to native freshwater mussels. In a two year study conducted with several species of

endangered or threatened mussels in various lifestages (glocchidial, juvenile, and adult) malathion exposure was tested at concentrations as high as 500,000 ppb. Adults were not significantly effected at up to 350,000 ppb. LC50 values for glocchidia were determined to range from 133,000 to 494,000 ppb. Juvenile LC50 values ranged from 36,000 to 523,000 ppb. These values have not been monitored nor are they predicted to occur in most environmental scenarios.

In a study of the effect of aerially applied malathion to juvenile brown and white shrimp, *Penaeus aztecus* and *Penaeus setiferus*, Conte and Parker (Texas A&M University, 1975) reported varying rates of mortality in relation to type of site and time after application for water concentrations which ranged from 2.0 to 3.2 ppb immediately after application. 3 Bayous and an estuarine lake were monitored. Mean water depth was 61 cm. Wild caught shrimp placed in cages were aerially sprayed at a rate of 85.7 g/hectare by aircraft at a speed of 145 km/hr. 7 to 3 passes were made at each site. In Test I within 9 hours after treatment 73% of all mortality occurred (24 of 50 shrimp died). Test II produced 50% mortality in 49 hours after application. Only 12% mortality occurred in Test III (estuarine lake).

Mortality of post larval and juvenile shrimp from exposure to malathion under laboratory and field conditions was examined by Proctor, Corliss, and Lightner of the National Marine Fisheries Service's Galveston Laboratory in 1966. Postlarval white shrimp and brown shrimp were exposed for 48 hrs. in laboratory tanks and caged shrimp were exposed in estuarine areas to application of malathion (95% ai) at 77.8 ml/acre. Water depth during the field study was about 1.2 meters (high-tide) for the first application and 0.3 meters at the time of the second application (mean tide). In the laboratory study the calculated 50% lethality levels for adults were 25.5 to 21.3 ppb for post larval brown shrimp and 100% mortality of larvae was seen at concentrations as low as 18 ppb.

In the field, environmental concentrations reached 8.9 ppb at high tide and 69 ppb at mean tide level. Some contamination of control areas occurred possibly from drift. 14% mortality was observed in controls and 80% mortality was seen in the test marsh. In the second application 65-69 ppb residue levels were seen 6 hours after treatment. Initial mortality was 48% in treated area and 4% in control area. After 10 hours white shrimp mortality increased to 96% in treated area and 7% in control area at mid depth levels. By 24 hours the residue levels had decreased to 1.08 ppb. White shrimp caged on the bottom level showed a similar trend after second application. Brown shrimp mortality results were inconclusive as treated areas showed 55% mortality while controls showed 44% mortality. This study provides an interesting insight into the potential effects of application during various tidal cycles.

Tagatz (1974) observed the effects to fish and invertebrates from two types of ground applications of malathion near saltmarsh environments in northwestern Florida. Both thermal fog and ULV application were monitored. Malathion was applied during low tide with 2 week intervals between applications. Thermal fog was applied at 6 oz/Acre (Sept. & Oct 1972) to a saltmarsh pond with fuel oil carrier. The thermal fog application produced high mortality of adult grass shrimp after 7 days. Some reduced AChE levels were observed in fish. No mortality of blue crabs or juvenile sheepshead minnow occurred. Three applications of ULV formulation at

0.64 fl oz/Acre were made by truck mounted aerosol generator, with a 330 foot swath. Grass shrimp, blue crabs, and sheepshead minnow were exposed in 18" diameter polyethylene tubs. No adverse effects or treatment related mortality was observed for the exposed organisms. Residue levels were 0.28 - 0.34 ppb after the 3rd application.

#### **Eco-community Effects**

Bourquin (USEPA Gulfbreeze Laboratory, 1975) examined the microbial interaction with malathion in artificial saltmarsh ecosystems. Natural bacteria samples from uncontaminated marsh were added along with 10 ml of sea water and 10 gm of sediment to 250 ml flasks. 10 mg. aliquots of malathion in acetone were added every 7 days. Cultures were analyzed for malathion levels and compared to control vial residue levels. Increased salinity sped up the degradation process of the parent compound. However, malaoxon levels remained constant. Monocarboxylic acid and dicarboxylic acid levels increased. Conclusion was that chemical and microbiological processes will act to degrade the levels of parent malathion in saltmarsh environments.

In a 1970 study effects of malathion to a freshwater ponds community were observed (Kennedy and Walsh, USFWS, 1970). 12 ponds containing bluegills and channel catfish were exposed. Four applications were made at concentrations of 0.02 and 0.002 ppm over an 11 week summer period. Pond surface areas were 688 m² with average depth of 0.76 m. and volume of 602 m³. The observed 8-44% fish loss was not felt to be treatment related as controls also had similar losses. The major treatment related effects appeared to be reductions of aquatic insects particularly midges at high and low doses (0.02 ppm and 0.002 ppm). Mayflies were reduced also with a significant reduction occurring after the 3rd application.

In a 1981 study investigating potential impact on fish and wildlife during aerial malathion applications in South San Francisco Bay region the California Fish and Game Department Pesticide Investigation Unit, (Water Pollution Control Laboratory) summarizes extensive monitoring performed during 1981 Medfly control programs. In general, most of the 200 fish and invertebrate tissue samples taken contained no detectable levels of malathion residues (<0.5 ppm). This was not true in the case of samples taken at fish kill sites. Steelhead trout populations were monitored in the San Lorenzo drainage area. Aquatic insect populations in the drainage were also monitored (number per sq. Cm). No discernable effects were noted for steelhead trout populations or appearance or size measurements when compared to control sites. There were significant reductions in either diversity or population counts for aquatic insects (33-50% reduction). Eight fish kills were associated with malathion spraying efforts, while 15 were either not determined as to cause or not attributed to malathion (see incident report section of this document). Many of the fish losses were sticklebacks (highly sensitive to malathion) while carp and channel catfish appeared unaffected at the same locations (Finlayson, B.J., G. Faggella, H. Jong, E. Littrell, and T.Lew, 1981).

The effects of malathion on fish and aquatic invertebrate communities in Stewart Creek, Fayette County, Alabama were monitored following applications for control of bollweevil in adjacent cotton fields. The Creek is located in west-central Alabama near Winfield and has an

approximately 11 square mile drainage basin. Samples were taken upstream, at the entry point, and 0.5 mi. downstream from the application site on two small cotton fields (7.6 and 11.6 acres). Fields were within 25 feet of the stream bank. There were no trees along the banks, only grasses and kudzu vines. Sample sites were sampled for three years-the first two during malathion applications, the last during which malathion was not applied. Captured fish were identified, counted, and some analyzed for AChE inhibition. Invertebrates were captured (by kicking up sediments into a dipnet), recorded, and then preserved in ethanol. 39 samples from each location were taken over a 34 month period. Only one sample date represented prespray conditions.

Concentrations recorded ranged from ND to 10.89 ppb (mean=3.49 ppb) for the nine 1993 applications and from 0.88 to 31.1 ppb (mean=2.08) during the four 1994 applications.. 11,921 fish of 48 different species were collected during the study. Numbers and diversity of collected fish did not appear to significantly vary. Not all species were equally distributed at the three sites and some population differences may be attributable to the differences in habitat preferences and availability at the three sites. Numerous specimens of rough shiner, *Notropis baileyi* were collected and analyzed for AChE and significant depression was noted during the spray periods when compared to the upstream control site. Of interest is the observation that downstream activity levels were lower than those at the application site.

Aquatic invertebrate populations which were collected included 87 taxa, and a total of 6,088 individual organisms. Some difference is apparent in numbers and diversity of species collected near the spray site when compared to the upstream site, but significant differences were less apparent at the downstream location. The upstream location did have more taxa present, however, than either of the other two sites for all periods of this study. The study author was not certain that this could be attributable to malathion influence as natural variability could also have played some part. (Kuhajda, B.R. et al, Dept. Of Biological Sciences, University of Alabama, 1996).

# Freshwater, Estuarine and Marine Aquatic Incidents:

The Agency receives and reviews all wildlife incidents where aquatic organism kills occurred following application of a pesticide or mixture of pesticides. These incidents are sometimes reported under 6a2 provisions of FIFRA while others are independently submitted by local, state, or federal agencies. Those which areassociated with malathion use in the area of the kills are summarized below along with factors which are known about events preceding the incident.

Table 27. Freshwater, Estuarine and Marine Aquatic Incidents.

Location and Date   Incident #	Description	Probability
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		10.01	
Florida Medfly report- 1997 Spray operations Hillsborough Area USDA Report	6 reports from 7/29- 8/28	40 Sites of Fish kills investigated-malathion detected in varying amounts in ponds and pools. Fish species effected include-various sunfish, bass, perch, and carp. 3 tropical fish farms hit. Mortality ranged from 5 to 1000 fish per site. Aerial drift generally blamed though some runoff events did occur.	Probable-residues detected in water and sometimes tissues
South Dakota, Minihaha Co., 7/6/87	I000804-025	10,000 dead fish-incl. walleye and yellow perch-aerial-Clean Crop -near Lake Madison	Probable
North Carolina, Wake Co., 5/17/73	B0000-225	10,000 panfish killed from ½ gallon spill of formulation(12.2 % Malathion/12.2% endosulfan into a pond.	Highly probable
Mississippi, Silver Creek, 7/6/89	I000389-001	166 fish, mostly carp, were killed-pest control company applied Aqua Malathion 8 in area	Possible
Missouri, 5/5/70	I000636-002	33 fish kill reports-one sick dog from ingestion of contaminated water	Possible
South Dakota, 7/3/87	I000804-025	35 other incidents besides Lake Madison fish kill-birds, fish, bees effected	Possible
Alabama	1002059-002	2 fish kills-Cotton field application of malathion-bass and sunfish killed	Possible
Florida	1000524-008	Turtle and birds mortalities reported	Possible
New Jersey, Delaware River 8/9/91	none-	Malathion distributed in sewage effluent to kill flies-15 gal malathion product /13000 gal effluent-1000 to 5000 white perch killed at discharge point	Probable
Maryland, Cherry Hill-5/12/80	EPA report	350 fish found dead- 10,000 acre lake- municipal pest control - Malathion	Probable
Missouri, Wentzville 6/29/80	EPA report	6,790 dead fish counted-Malathion treated municipal sewage discharge to McCoy Creek	Probable
South Carolina, Hilton Head-5/25/81	EPA report	1500 dead fish-Sea Pine Lagoons-estuary- pesticide spraying operations using Malathion	Probable
Virginia, Norfolk- 8/14/81	EPA report	1500 dead fish-Mason Creek-industrial operations using Malathion	Possible
Florida, near Miami - Summer, 1956	Old report from Mr. J.E. McCurdy- Florida Mosquito Control?	Extensive observations of numerous canals, ponds, ditches, and pools after aerial application of Malathion-some species killed others not-mortality to thousands of mojarra silversides was immediate after spraying-snook, mollies, cyprinids, pinfish, bass and killifish also killed in ditch and canal areasstrangely gambusis were not sensitive	Probable

Massachusetts-four incidents White Island Pond near Plymouth Glen Charles Pond near Waneham Waneham River-estuary Agawan River-estuary	6a2 Report from American Cyanamid Oct. 4, 1990 #281720	4 fish kills reported from treatment of 700,000 acres of estuarine areas with Malathion for control of mosquitoes. Many of the dead fish were estuarine killifish species.	Probable
New York, Thornwood-5/14/84	EPA report	500 dead fish-Pond in Carroll parkagriculture operations using malathion adjacent to pond	Possible
California-Monitored aquatic incidents during broadscale aerial application over San Francisco, Bay area ,1981. Administrative Report 82-2, Dept. Of Fish and Game, Environmental Services Branch, 1982.	Medfly Control	23 fish poisoning incidents were investigated-8 were confirmed as caused by malathion -10 were listed as undetermined causes-2 were caused by chlorine discharge at sewer plants. Malathion incidents included observed mortality of over 2300 fish including stickleback(Stevens, San Tomas Aquino, Pescadero Creeks), carp(Adobe and Mission Creeks), mosquitofish(Mission Creek), topsmelt, flounder, striped bass, and gobies(Seal and Redwood Creek, and Mayfileld Sloughs), and largemouth bass and crappie in San Jose Pond.	Probable- Malathion residues detected in water- tissue concentrations in gill filaments, liver, skeletal muscle and whole body tissues

	Hab t /t bina		D 1 11
Alabama, Tennessee 1995 Southeast Bollweevil Eradication Program, Environmental Monitoring Report	USDA /APHIS 1995 report	Leighton, Alabama-Catfish Farm-dead catfish-600 ft from aerially treated field(#295) Lincoln Co., TN2 acre stream fed pond-4 cotton fields upstream-dead bass, catfish, sunfish.	Probable- inspection was too late in many cases-1 week after
		Lighten, ALBig Nance Creek-30,000-40,000 fish	Possible- Endosulfan, malathion and methyl parathion all suspect.
		Colbert Co.,ALDonnegan's Slough-fish kill- both followed heavy rains 8/4-8/8 resulting from hurricane	Probable-
		Fish pond near Site 139-dead sunfish, catfish-malathion residues in water-5 to 6 ppb	Probable
			Possible
		Catfish Farm-2 ponds-dead catfish near field #19-150 feet from ponds-9 old day samples did not show high concentration levels-only trace levels	
		Fishkill-1/10 acre pond near field #303-dead adult catfish sampled-malathion detected in water.	Probable-fish tissue residues 35-85 ppb.
		Fish, turtle, frog, and crayfish kill-5 acre wetland-2 to 3 ft. Depth-cotton field 503 located 600 ft. away-drainage ditch leads to wetland-6 day old samples-malathion still detected in water and fish tissues.	Probable-though not likely from bollweevil aerial treatment, 6 weeks previous
Alabama, Tennessee 1995 Southeast Bollweevil Eradication Program, Environmental Monitoring Report	USDA /APHIS 1995 report	Fish Kill(bass, sunfish, catfish)-8 acre pond-20 ft. From application site(cotton field # 1180)-residues of 77.8 ppb in one water sample. Other chemicals used in area-Larvin and Pyrat	Probable-residue levels in tissues were high
(continued)		Fishkill -1/4 acre farm pond near cotton fields #118 and 119-malathion residues in all 4 water samples-fish tissue sample contained 351ppb malathion.	Possible-sampling too late-cotton field treated 8 days earlier
		Fishkill(catfish)-1/4 acre pond near field#166-70 ft from pond-malathion detected in 8 day post-application samples-	

California-4 Incidents	EPA report	2000 dead fish-Fremont Creek-crop	Possible
near Fremont, Loma		treatment	
Mar, San Jose, and San		200 dead fish-Pescadero Creek-crop	
Mateo Co. 9/30/81-		treatment	
10/9/81		75 dead fish-pond near San Jose-crop treated	
		12 dead fish-Adobe creek-crop treatment	

### **Significance of Reported Incidents**

Though malathion has been used for many years, the greatest numbers of detailed reports of fish kill incidents involved heavily monitored programs such as USDA's boll weevil eradication program and the mediterranean fruit fly eradication efforts. Other incidents appeared linked to uses near aquatic habitats where direct drift may have occurred, such as mosquito control. In many of the incidents use rates and residue levels following the incidents are not clear and kills are investigated days after the event probably occurred. In two of the incidents sewage discharge was treated with malathion to control flies and then released directly into tributaries. In all cases where residue levels are provided they are within the limits expected to prove toxic to sensitive fish species (>4 ppb). One of the points that should be included when discussing fish kill incidents is that invertebrates are likely to have been more severely effected since fish are less sensitive to malathion than a majority of the invertebrate species tested in laboratories to date. In most of the fish kill incidents there appears to have been no effort to investigate the effects to the other components of the ecological community in the adversely effected sites.

## **Toxicity to Plants**

To date the Agency has received no data from malathion registrants regarding the toxicity of malathion to non-target plants. This is not normally a requirement for insecticidal use pesticides. However, the direct application of malathion to aquatic habitats does raise concerns regarding possible phytotoxicity of the product impurities or inert ingredients to non-target aquatic plants or semiaquatic plants. Based on the following study and also results observed in field studies (see previous study, MRID 00104629-Giles, 1970) malathion is expected to be taken up and stored for some time in plant tissues. Metabolites may later show up in new stem and leaf growth.

Bourke, J.B. (1968) examined the comparative metabolism of malathion -  $C_{14}$  in plants (as well as animals). Red Kidney bean plants were forced to imbibe radio labeled malathion solution by passing air over foliage for 20-30 minutes (with solution mixed into air stream?)  $C^{14}$  was traced in tissues of plants for 14 days. Various intermediates (metabolites) were deposited within tissues. Plants appeared to store various metabolites in tissues..

# **Toxicity of Degradates and Impurities**

Malathion may contain impurities which account for up to 5% of the pesticide content. These impurities include diethyl fumarate, diethylhydroxysuccinate, O,O-dimethylphosphorothioate, O,O,O-trimethyl phosphorothioate, O,O,S-trimethyl phophorodithioate, ethyl nitrite, diethyl-bis (ethoxycarbonyl)mercaptosuccinate, S-1, 2-ethyl-O,S-dimethyl phosphorodithoate (isomalathion),

S-(1-methoxycarbonyl-2-ethoxycarbonyl)ethyl-O, O-dimethyl phosphorodithoate, Bis-(O,O-dimethyl thionophosphoryl) sulfide, Diethyl methylthiosuccinate, S-ethyl-O,O-dimethyl phosphorodithioate, S-1,2-bis(ethoxycarbonylethyl-O,O,-dimethyl phosphorothioate (malaoxon), diethyl ethylthiosuccinate, and sulfuric acid. These impurities may range from 0.5% to 1.0 % of the content and have been shown to be toxic alone and may even potentiate the toxicity of the parent. Pellegrini and Santi, 1972, found that purified malathion (98% ai) was actually less toxic to laboratory rats than technical malathion of 92.2% purity with corresponding LD50 levels of 1580 mg ai/Kg versus 8000 mg ai/Kg, respectively.

Several studies regarding the toxicity and retention of degradates in fish were reviewed from literature. In 1976 studies at the EPA Gulfbreeze Laboratory, Cook and Moore found that the monocarboxylic and dicarboxylic acids of malathion were detected in fish tissues after 24 hours, but malaoxon and malathion were not. Studies by Dr. Michael Bender at the University of Michigan (1969) and Virginia Institute of Marine Sciences (1976) showed that diethyl fumarate and 2 mercapto diethyl succinate were more toxic than the parent compound to fathead minnow and eastern mudminnows (see pages 71-72). However the percentage of these degradates in the environment is expected to be low enough(<10% of original parent) to prevent additional toxicity to fish. Unfortunately, the testing reported for degradate toxicity was not performed on fish species considered highly sensitive to malathion (fathead minnow and eastern mudminnow). No degradate toxicity to invertebrate species has been reviewed. Toxicity from acculmulation of degradates following multiple applications is unclear without further fate and chemistry data to characterize their potential to degrade in the environment.

# **Toxicity of Dual Active Mixtures**

#### **Mixture Toxicity to Terrestrial Wildlife**

Malathion and Methoxychlor mixtures are manufactured by Cheminova and Platte Chemical Company. Only Platte Chemical Co. markets this product in the U.S. There is some data regarding the possibility of increased toxicity of combinations of pesticides to rats and mice(M.L. Keplinger and Deichmann, 1967). In their paper entitled Acute Toxicity of Combinations of Pesticides (Toxicology and Applied Pharmacology 10, 586-595(1967), Keplinger and Deichman tested numerous mixtures of pesticides commonly used at the time. Rats and mice were orally intubated with pesticides mixed in corn oil. Generally 5-7 dosages were administered to five animals at each level, with separate chemicals administered within 10 seconds of each other. When methoxychlor was mixed with malathion there was a slight additive effect to expected toxicity, based on the author's computation, which assumed that the expected LD50 of the combined chemicals would be equivalent to the midpoint between the known oral toxicities of the two compounds alone. The expected LD50 of methoxychlor/malathion 50-50 mix was estimated to be 1850 mg/Kg for mice whereas the actual observed LD50 was 1620 mg/Kg. This may be an inadequate difference on which to base any gross assumptions of synergistic effect for these two chemicals in combination. However, it should be noted that certain other combinations of malathion did show additive effects (toxaphene and carbaryl) whereas a protective effect was noted with certain other combinations (aldrin, dieldrin, chlordane, and endrin) when the same assumptions for predicted LD50 levels were made.

Malathion is formulated with several other active ingredients which also may display some levels of toxicity to birds. Among these is Fertilome A-C-G Insecticide and Fungicide Mix marketed by Voluntary Purchasing Group Inc., Blackleaf Liquid Fruit Tree Spray with Fungicide (Sureco Inc.). These formulations may have additional toxicity over single active formulations containing only malathion and should be tested separately. At this time the Agency has no data on which to predict potential effects to birds from aggregate exposure to these multi-active formulations. Comparison of methoxychlor and malathion avian toxicity values (see table below) indicates that methoxychlor displays low acute values similar to malathion. The mixture of these compounds may provide some additional exposure time due the increased persistence of methoxychlor over malathion. The reviewer was unable to locate data to indicate that the mixture will or will not be more toxic due to synergistic effects of the two insecticides. The fungicide/insecticide mixtures may also add additional toxicity to avian species. This is based on slightly elevated plasma butyryl cholinesterase (BChE) levels in quail when malathion was administered in combination with vinclozolin and ketoconazole and elevated BChE levels in rats when malathion was administered in combination with propiconazole, vinclozolin, and clomitrimazole (Martin, J.J.R. and Thomas Badger, University of Arkansas, Toxicology and Pharmacology 130, 221-228,1995). In studies with Japanese quail, red-legged partridge, and pigeons pretreatment with the fungicide prochloraz resulted in enhanced toxicity of malathion (Riviere J.L. et al, Arch. Environmental Toxicology 14, 1985 and Johnston, G. et al., 1989 Pesticide Biochem. Physiology 35, 107-118)

Table 28. Comparative Toxicity of Malathion and Methoxychlor to birds.

Species	% ai	Malathion	% ai	Methoxychlor
Mallard	95%	LD50=1485 mg/Kg	Tech	LD50=2000 mg/Kg
Ring-necked Pheasant	95%	LC50=2639 ppm	Tech	LC50>5000 ppm
Bobwhite	95%	LC50=3497 ppm	Tech	LC50>5000 ppm

Mixtures containing malathion and methoxychlor may produce similar or more pronounced chronic effects if additional persistence results from addition of the organochlorine insecticide.

#### **Mixture Toxicity to Aquatic Organisms**

Studies published by the Bureau of Sport Fisheries and Wildlife(later USFWS) in the June 1970 issue of Progress in Sport Fishery Research 1969, explored the synergistic activity of combinations of pesticides on toxicity levels for bluegill and rainbow trout. Synergism was observed when malathion was mixed with baytex, EPN, Parathion, Perthane, and Carbaryl. Additive effect was noted when combined with DDT and Toxaphene.

Review of toxicity data for methoxychlor indicates that this chemical may provide additional toxicity over that of malathion to most species of aquatic organisms. A brief, but not

comprehensive, comparison table is presented below for comparison of acute toxicity values for the two insecticides to fish and invertebrates. The Agency has not received data to support the registration of methoxychlor/malathion mixtures.

Table 29. Malathion / methoxychlor comparative toxicities to aquatic organisms

Species	%ai	Malathion	%ai	Methoxychlor
Waterflea, Daphnia pulex	95	EC50=1.8 ppb	98	EC50=0.78 ppb
Scud, Gammarus fasciatus	95	EC50=0.5 ppb	98	EC50=1.9 ppb
Scud, Gammarus lacustris	95	EC50=1.8 ppb	98	EC50=0.8 ppb
FW shrimp, Palaemontes kadiakensis	95	LC50=12 ppb	98	LC50=1.05 ppb
Waterflea , Simocephalus serrulatus	95	EC50=0.59 ppb	98	EC50=5.0 ppb
Seed shrimp, Cypidopsis vidua	95	LC50=47 ppb	98	LC50=32 ppb
Blue crab, Callinectes sapidus	95	LC50>1000 ppb	100	LC50=320 ppb
Oyster, Crassostrea virginica	95	EC50>1000 ppb	100	LC50=90 ppb
Sowbug, Asellus brevicaudus	95	LC50=3000 ppb	98	LC50=34 ppb
Cutthroat trout, Oncorhynchus clarki	95	LC50=1740 ppb	98	LC50=6.2 ppb
Yellow perch, Perca flavens	95	LC50=263 ppb	98	LC50=17.5 ppb
Channel catfish, Ictalurus punctatus	95	LC50=7620 ppb	98	LC50=52 ppb
Bluegill sunfish, Lepomis macrochirus	95	LC50=20 ppb	98	LC50=32 ppb
Rainbow trout, Oncorhynchus mykiss	95	LC50=4 ppb	98	LC50=11 ppb
Spot, Leiostomus xanthurus	95	LC50=320 ppb	100	LC50=23 ppb

Based on the data reviewed thus far for the two chemicals it would appear that the mixture may prove more toxic to most species of aquatic organisms if based on an equivalent active ingredient % of malathion alone. There will, however, be species sensitivity differences in some instances.

# **Ecological Risk Assessment**

## **Exposure and Risk to Nontarget Terrestrial Wildlife**

The acute risk quotients for broadcast applications of nongranular products are tabulated below. They are based on estimated acute and chronic residue levels calculated in the terrestrial exposure portion of this document divided by the LC50 or chronic NOEC of the most sensitive species tested.

#### 1. Birds

Avian Acute and Chronic Risk Quotients for Single Application of Nongranular Products (Broadcast or Foliar Spray) are based on the most sensitive species ringneck pheasant LC50 of 2639 ppm and the chronic NOEC for bobwhite quail of 110 ppm.

Multiple application scenarios were estimated using a first order dissipation program incorporating Fletcher values in conjunction with the appropriate half-life values. The high exposure scenario for each application rate is reflected in the table, that is the minimum interval and maximum number of applications permitted under tolerance testing for this crop group. A mean foliar dissipation half-life of 5.5 days was inputed into the program, based on monitored values from several studies including USDA bollweevil and medfly programs and research efforts by Willis and McDowell, 1987 (referenced in previous terrestrial exposure section). Samples of the actual outputs are included as addendums to this document.

The risk quotient results indicate that for broadcast applications of nongranular products, avian acute high (0.5), restricted use (0.2), and endangered species (0.1) levels of concern are exceeded at registered multiple application rates equal to or above 3.75 lb ai/A , 2.0 lb ai/A and 0.94 lb ai/A , respectively.

Table 30 Avian Acute Dietary Risk Quotient Ranges

Cheminova and IR4 Supported Maximum Tolerance Rates and Scenarios on Grasses-

Seed

	Folia	ar Dis	sipation T	1/2=5.5 D	ays Nun	ber of A	Applicat	ions					
	Rat e	Int	1 grass-seed	2	3	4	5	6	7	8	9	10	12- 25
A	0.17 5	7D	0.01-0.0004									0.02- 0.001	
В	0.50	NA	0.04-0.001										
С	0.61	5D	0.05-0.001				0.11- 0.007						
C	0.61	7D	0.05-0.001	0.07- 0.003	0.09-0.005								
C	0.61	14 D	0.05-0.001	0.06- 0.004									

D	0.76	10 D	0.06-0.002				0.09- 0.006						
E	0.94	3D	0.08-0.002										
E	0.94	6D	0.08-0.002					0.15- 0.01					
E	0.94	7D	0.08-0.002		0.13-0.008				0.15- 0.01				
F	1.0	7D	0.09-0.002					0.15- 0.01					
G	1.25	3D	0.1-0.003	0.19-0.01				0.32- 0.02					
G	1.25	5D	0.1-0.003				0.23- 0.014						
G	1.25	7D	0.1-0.003		0.17-0.01	0.19- 0.01	0.19- 0.01	0.19- 0.01	0.19- 0.01	0.19- 0.01	0.19- 0.01	0.19- 0.01	0.19- 0.01
G	1.25	14 D	0.1-0.003	0.13- 0.008									
Н	1.50	7D	0.13-0.003		0.21-0.01			0.23- 0.01					
Ι	1.56	7D	0.14-0.004	0.16- 0.006			0.23- 0.01						
J	1.88	5D	0.17-0.004					0.36- 0.02					
J	1.88	7D	0.17-0.004		0.27-0.02	0.28- 0.02		0.29- 0.02					
J	1.88	14 D	0.17-0.004	0.2-0.01									
K	2.03	6D	0.18-0.005					0.34- 0.02					
K	2.03	7D	0.18-0.005		0.29-0.02	0.30- 0.02							
L	2.5	3D	0.22-0.006		0.5-0.02								0.7- 0.04
L	2.5	5D	0.22-0.006		0.42-0.03								
L	2.5	7D	0.22-0.006		0.36-0.02		0.38- 0.02						
M	3.43	5D	0.31-0.009				0.42- 0.02						
N	3.75	7D	0.34-0.01			0.56- 0.02		0.58- 0.04					
N	3.75	14 D	0.34-0.01										
o	4.7	30 D	0.42-0.01	0.43-0.01									
P	5.0	7D	0.45-0.01	0.64-0.01	0.72-0.3	0.75- 0.03							

Q	6.25	30 D	0.57-0.02		0.58-0.01							
0.175			10=Orange, Grap	efruit, Lemon,	Lime, Tangeri	ne, Tangelo, a	and Kumquat	t				
0.50 II		_	<b>1</b> =Flax									
0.61 ll	ai/A		<b>C5(5D)</b> =Sweet Co				Rice, Sorgh	um, Wheat,	and Rye			
			<b>22(14D)</b> =Alfalfa,	Clover, Lespec	deza, Lupine and	d Vetch						
0.76 ll			5=Blueberry									
0.94 11	ai/A		(3D)=Grass for	•	Mushroom, E	<b>6(6D)</b> =Straw	berry, <b>E3(7</b> )	D) =Pepper	mint and s	pearmint,		
			27(7 <b>D</b> )=Macadam									
	,		lons, Watermelon,				_				~	
1.25 ll	ai/A		G1(3D)=Grass for	•		, ,						
			<b>G25(3D)</b> =Cotton,						•		, ,	• •
			JLV), <b>G5(7D)</b> =T									
			Cabbage and Cherr	•					. ,	_	U(7 <b>D</b> )=Pea	ars and
1511.	<b>:</b> / A		Quince, G12(7D)		apaya, G2(14D	)=Airaira, Ci	over, Lupine,	, vetch and	Lespedenz	za		
1.5 lbs			12(7D)=Celery, H		<b>7D</b> \ O-: C-	l: - Cl11-4	T1					
1.56lb			2(7 <b>D</b> )=Potato, Sw					Dl		C	_	
1.88 ll	) al/A		6(5 <b>D</b> )=Lettuce, <b>J</b>	. ,				y, Dewberry	, Currant,	Gooseberry	/,	
2 02 1	bs ai/A		3(7 <b>D</b> )=Cucumber			•		.1 1 C	: Cl			
2.03 1	DS al/A		<b>K6(6D)</b> =Strawberr	•	· , .			•		,		
2 50 11	2 / A		(4(7 <b>D</b> )=Blackberr		•		•	•	•			
2.50 11			25(3D)=Cotton, I		, ,	ras, wainuts,	and Pecans,	L3(/D)=F	reas			
3.43 II 3.75 II			<b>M5(5D)</b> =Tomato,	11		(14D)_Doork	and Mastari					
			<b>14(7D)</b> =Apricots,	No(7D)=Cne	rry, N4	( <b>14D</b> )=Peach	and Nectari	ne				
	ai/A O2(3			Thostmuts								
			eapple, <b>P4(7D)=</b> 0		omon Limo To	a.i.a.a.a.d.f	Fomoslo					
6.25 ll	) al/A	•	<b>(30D)</b> =Oranges	, Graperruit, L	emon, Lime, 18	ingerine and	i angeio					

Chronic risk quotients can be calculated based on the average residues on food items. Average residues result from the pesticide being applied repeatedly, but degrading over the course of time from the first application to the last application. Due to rapid malathion degradation characteristics, high numbers of applications and minimal intervals in many cases, birds are expected to be exposed to continuous peaks at 3, 5, 6, 7, or 10 day intervals. Avian chronic risk quotients based on average residues for multiple, broadcast applications of non-granular products may not be as pertinent under this type of scenario, therefore maximum peaks were compared against the NOEC for bobwhite quail chronic test results. The results, depicted in the table which follows, indicate that for multiple broadcast applications of nongranular products based on expected peak residues, the avian chronic level of concern is exceeded at a registered maximum application rate equal to or above 0.5 lb ai/A on grasses (based on the assumption of chronic effects due to repeated exposure to peak residues with less than one week intervals). This chronic level could be maintained by continuous and repetitive applications during a crop season.

Table 31. Avian Chronic Risk Quotient Ranges
Cheminova and IR4 Supported Maximum Tolerance Rates and Scenarios on Grasses-Seeds

	Foliar Dissipation T1/2=5.5 Days Number of Applications												
	Rate lb ai/A	Int. Day	1	2	3	4	5	6	7	8	9	10	12- 25
A	0.17 5	<b>7</b> D	0.4-0.01									0.7- 0.04	
В	0.50	NA	1.09-0.03										
С	0.61	5D	1.3-0.03				2.7-0.17						
С	0.61	7D	1.3-0.03	1.7-0.08	2.1-0.12								
С	0.61	14 D	1.3-0.03	1.6-0.1									

D	0.76	10 D	1.7-0.05				2.3-0.14						
E	0.94	3D	2.0-0.06										
Е	0.94	6D	2.0-0.06					3.8-0.05					
E	0.94	7D	2.0-0.06		3.2-0.2				3.5-0.2				
F	1.0	7D	2.18-0.06					3.7-0.22					
G	1.25	3D	2.72-0.08	4.6-0.3				7.8-0.5					
G	1.25	5D	2.72-0.08				614-38						
G	1.25	7D	2.72-0.08		4.3-0.3	4.4-0.3	4.6-0.3	4.6-0.3	4.6-0.3	4.6-0.3	4.6- 0.3	4.6- 0.3	4.6- 0.3
G	1.25	14D	2.72-0.08	3.2-0.2									
н	1.50	7D	3.3-0.09		5.2-0.33			5.5-0.34					
I	1.56	7D	3.4-0.1	3.9-0.14			5.7-0.35						
J	1.88	5D	4.1-0.11					8.6-0.5					
J	1.88	7D	4.1-0.1		6.5-0.4	6.8-0.4		7.0-0.4					
J	1.88-	14 D	4.1-0.1	4.8-0.3									
K	2.03	6D	4.4-0.1					8.2-0.5					
K	2.03	7D	4.4-0.1		7.0-0.4	7.3-0.45							
L	2.5	3D	5.45-0.2		11.7-0.5								17- 1.1
L	2.5	5D	5.45-0.2		10.1-0.6								
L	2.5	7D	5.45-0.2		8.6-0.5		9.1-0.6						
M	3.43	5D	7.6-0.2				9.2-0.6						
N	3.75	7D	8.1-0.24			13.5-0.6		13.9-0.9					
N	3.75	14 D	8.1-0.24										
О	4.7	30 D	10.2-0.3	10.4-0.3									
P	5.0	7D	10.9-0.3	15.4-0.4	17.3-0.6	18.1-0.7							
Q	6.25	30 D	13.6-0.4		14.0-0.4								

0.175 lbai/A A10=Orange, Grapefruit, Lemon, Lime, Tangerine, Tangelo, and Kumquat

0.50 lb ai/A B1=Flax

0.61 lb ai/A C5(5D)=Sweet Corn, C2(7D)=Hops, C3(7D)=Beans, Corn, Rice, Sorghum, Wheat, and Rye,

C2(14D)=Alfalfa, Clover, Lespedeza, Lupine and Vetch

**0.76 lb ai/A D5**=Blueberry

0.94 lb ai/A E1(3D)=Grass for hay, E4(3D)=Mushroom, E6(6D)=Strawberry, E3(7D) =Peppermint and spearmint,

E7(7D)=Macadamia

1.0 lb ai/A F6(7D)=Melons, Watermelon, Pumpkin and Winter Squash

1.25 lb ai/A

G1(3D)=Grass for hay, G2(3D)=Field corn, G2(7D) Brussel sprouts, cauliflower, collards, kale, kohlrabi G6(3D)=Mustards, G25(3D)=Cotton, G5(5D)=Watercress, G3(7D)=Rice, Sorghum, Wheat, Rye, Barley, Oats and Corn, G4(7D)=Blueberry(ULV), G5(7D)=Turnip, Broccoli, Apple, Sweet Corn, Beet, Horseradish, Parsnip, Radish, Rutabaga, Salsify, Sweet potato,

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G6(7D)= Cabbage and Cherry(ULV), G7(7D)=Carrot, G8(7D)=Mango and Passion fruit, G9(7D)=Asparagus
G10(7D)=Pears and Quince, G12(7D)=Guava and Papaya, G2(14D)=Alfalfa, Clover, Lupine, Vetch and Lespedenza
H2(7D)=Celery. H6(7D)=Okra
```

1.5 lbs ai/A

1.56lbs ai/A I2(7D)=Potato, Sweet potato, I5(7D)=Onion, Garlic, Shallot, Leeks

J6(5D)=Lettuce, J4(7D)=Blackberry, Raspberry, Loganberry, Boysenberry, Dewberry, Currant, Gooseberry, 1.88 lb ai/A

J3(7D)=Cucumber, Chayote, J6(7D)= Strawberry, J2(14D)=Grapes

2.03 lbs ai/A K6(6D)=Strawberry(50%WP), K3(7D)= Spinach, Dandelion, Endive, Parsley and Swiss Chard,

K4(7D)=Blackberry, Raspberry, Gooseberry, Loganberry, Dewberry, Currant and Boysenberry L25(3D)=Cotton, L3(5D)=Figs, L3(7D)=Mustards, Walnuts, and Pecans, L5(7D)=Peas

M5(5D)=Tomato, Pepper, Eggplant 3.43 lb ai/A

3.75 lb ai/A N4(7D)=Apricots, N6(7D)=Cherry, N4(14D)=Peach and Nectarine

4.7 lb ai/A O2(30D)=Avocado

5.0 lb ai/A P3(7D)=Pineapple, P4(7D)=Chestnuts

Q3(30D)=Oranges, Grapefruit, Lemon, Lime, Tangerine and Tangelo 6.25 lb ai/A

## Mammals

2.50 lb ai/A

Birds and mammals have similar responses to xenobiotics. Birds have lower hepatic microsomal mono-oxygenase and A-esterase activity than do mammals. Therefore, birds are more susceptible than mammals to both organophosphate and carbamates in general. Malathion does not present an acute risk to mammals based on the low toxicity observed in exposure studies conducted with laboratory rats, rabbits and mice.

However, malathion does present a potential for long-term dietary exposure to mammals if multiple applications are repeated with inadequate intervals to allow for complete degradation. Malathion does appear to offer potential chronic hazard to birds, but hazard to mammals appears to be less likely. In 2 year oncogenic studies with laboratory rats (Food and Drug Research Labs, 1980-ACC 248179-180) the animals were fed diets containing 0, 1000 and 5000 ppm of 92.1 % malathion. No gross adverse effects were noted, however decreased cholinesterase levels and body weight were noted at 1000 ppm test levels. In another study male and female rats were fed 4000 ppm of malathion in their diets (equivalent to 240 mg/kg/day) for five months. Reduced litter size and survival of young was observed in this study (Kalow and Marton, 1965). These effect levels are above those expected on vegetation from the highest rate scenario (1500 ppm on vegetation surrounding citrus at 6.25 lb ai/A). However, temporary reduction of acetocholinesterase levels is expected at higher rates of application.

Estimating the potential for adverse effects to wild mammals is based upon EEB's draft 1995 SOP of mammalian risk assessments and methods used by Hoerger and Kenaga (1972) as modified by Fletcher et al. (1994). The concentration of malathion in the diet that is expected to be acutely lethal to 50% of the test population (LC50) is determined by dividing the LD50 value (usually rat LD50) by the % (decimal of) body weight consumed. A risk quotient is then determined by dividing the EEC by the derived LC50 value. Risk quotients can then calculated for three separate weight classes of mammals (15, 35, and 1000 g), each presumed to consume four different kinds of food (grass, forage, insects, and seeds). The acute risk quotients for broadcast applications of nongranular products are tabulated using the equations below. The reviewer calculated quotients based on a full range of application scenarios, but not on every possible scenario. In addition larger mammals were not included as data suggests that toxicity thresholds will not be attained for the higher weight classes of mammals. As with the risk quotient for birds, the driving influence on how high field residues (and thus the risk quotients) will be from multiple appears to be determined by the interval between applications more than the total number of applications of malathion. Chronic exposure to malathion is more a matter of continuous exposure to peak levels on a 3, 5,

6, 7, or 14 day cycles. Intervals of less than 7 days may allow buildup of malathion residues levels over time. Unfortunately, many of the mammalian chronic studies conducted for human health analysis are two year studies which are not truly comparable to a single season exposure period expected for wild mammals. In many of the chronic mammal studies less noticeable sublethal effects were noted such as reduced acetocholinesterase levels, in brain, blood and plasma((Hazelton Labs, AMA Arc. Occ. MED:8; 1953) or gastric ulcers(Nat. Cancer Institute, 1979). These types of effects would go unnoticed during field use in all probability.

Mammalian (Herbivore/Insectivore) Acute Risk Quotients for Single and Multiple Application of Nongranular Products (Broadcast) Based on rat LD50 of 390 mg/Kg

$$RQ = \underbrace{EEC (ppm)}_{LD50 \text{ (mg/kg)/ \% Body Weight Consumed}} \text{ or } \underbrace{EEC}_{NOEC}$$

**Table 32. High Exposure Scenario RQ's for Dietary Consumption by Small Mammals:** Small Mammal-15 gram Wt consuming 95% of Food Matter as Shortgrass or Fruit Small Mammal of 35 gm Wt consuming 66% of Food Matter as Shortgrass or Fruit

Site/App. Method	Rate (lbs ai/A)	Single Application Day 0 Max. EEC Range for Short grass to Fruits	Highest # Applic. (Minimum Interval)	Multi- App. Max. EEC Range- Shortgrass to Fruit	Acute RQ Range 15 g Body Wt Consuming 95%	Acute RQ Range 35 g BodyWt Consuming 66%
Citrus/Aerial	0.175	42 to 1.2 ppm	10X(7D)	43 to 2.7	0.10- 0.006	0.07 - 0.0045
Corn/Aerial	0.61	146 to 4.3 ppm	3X(7D)	195 to 12	0.47 - 0.029	0.33 - 0.02
Blueberry/Aerial	0.76	182 to 5 ppm	5X(10D)	195 to 12	0.47 - 0.029	0.33 - 0.02
Strawberry/Ground	0.94	226 to 7 ppm	6X(6D)	278 to 17	0.67 - 0.04	0.47 - 0.02
Melons/Ground	1.0	240 to 7.5 ppm	6X(7D)	280 to 17	0.68 - 0.04	0.48 - 0.02
Cotton/Aerial	1.25	300 to 8.8 ppm	25X(3D)	531 to 33	1.3 0 - 0.08	0.90 - 0.056
Onion/Ground	1.56	374 to 11 ppm	5X(7D)	437 to 27	1.06 - 0.07	0.74 - 0.046
Lettuce/Ground	1.88	451 to 13 ppm	6X(5D)	601 to 37	1.46 - 0.09	1.01 - 0.06
Strawberry/Ground	2.03	487 to 14 ppm	6X(7D)	526 to 33	1.3 - 0.08	0.90 - 0.056
Cotton/Aerial	2.50	600 to 18 ppm	25X(5D)	733 to 35	1.78 - 0.09	1.24 - 0.05
Tomato/Ground	3.43	823 to 24 ppm	5X(5D)	1096-68	2.67 - 0.16	1.86 - 0.11
Cherry/Ground	3.75	900 to 26 ppm	6X(7D)	1050-60	2.56 - 0.14	1.78 - 0.10

Avocado/Ground	4.7	1128 to 33 ppm	2X(30D)	1128-35	2.75 - 0.08	1.91 - 0.08
Pineapple/Ground	5.0	1200 to 35 ppm	4X(7D)	1400-40	3.41 - 0.09	2.37 - 0.068
Citrus/Ground	6.25	1500 to 44 ppm	2X(30D)	1500-44	3.65-0.074	2.54 - 0.07

Table 33.

## Chronic RQ Ranges for Mammals - Exposure to Multiple/Continuous Residue Peaks

Based on Chronic Studies with Mice(MRID 242903) and rats (Document # 000389, Karlow and Marton, 1965) Reduced Body Wt. -Mice At 500 PPM Reduced Pup Survival for Rats at 4000 ppm

Site/Method Application	Rate (lb ai/A)	# of Apps. (Interval)	Maximum EEC Range in PPM	Chronic RQ Growth	Chronic RQ Reproduction
Citrus/Aerial	0.175	10X(7D)	43 to 2.7	0.09-0.005	very low
Corn/Aerial	0.61	3X(7D)	195 to 12	0.39-0.024	very low
Blueberry/Aerial	0.76	5X(10D)	195 to 12	0.39-0.024	very low
Strawberry/Ground	0.94	6X(6D)	278 to 17	0.55-0.03	low
Melons/Ground	1.0	6X(7D)	280 to 17	0.56-0.03	very low
Cotton/Aerial	1.25	25X(3D)	531 to 33	1.06-0.07	0.13-0.008
Onion/Ground	1.56	5X(7D)	437 to 27	0.87-0.05	very low
Lettuce/Ground	1.88	6X(5D)	601 to 37	1.2-0.07	very low
Strawberry/Ground	2.03	6X(7D)	526 to 33	1.05-0.07	very low
Cotton/Aerial	2.50	25X(5D)	733 to 35	1.46-0.07	0.18-0.009
Tomato/Ground	3.43	5X(5D)	1096-68	2.19-0.13	0.27-0.017
Cherry/Ground	3.75	6X(7D)	1050-60	2.10-0.12	0.26-0.02
Avocado/Ground	4.7	2X(30D)	1128-35	2.26-0.07	0.28-0.008
Pineapple/Ground	5.0	4X(7D)	1400-40	2.80-0.08	0.35=0.01
Citrus/Ground	6.25	2X(30D)	1500-44	3.0-0.09	0.38-0.01

### **Malathion Used in Bait Applications**

Though no granular malathion products are proposed for reregistration, malathion is used in a number of bait application uses. These liquid bait applications may be similar to granules in their route of ingestion by exposed wildlife. Mammalian species also may be exposed to bait droplets containing concentrated (95% ai) malathion. This would be applicable to such programs as the medfly eradication programs where malathion protease baits are employed to attract the target organisms (Mediterranean fruit fly). They also may be exposed by other routes, such as by walking on exposed bait and drinking water contaminated by malathion baits. The number of lethal doses (LD50's) that are available within one square foot immediately after application can be used as a risk quotient (LD50's/ft²) for the various types of exposure to bait pesticides. Risk quotients are calculated for a small mammal and for the ringneck pheasant.

### Mammalian Acute Risk Quotients for Bait Products (Broadcast).

Use SiteApplication MethodRate in lbs ai/A% Surface ResiduesMedfly ControlAerial0.1880% efficiency est.

Body Weight (g) Rat =100 gm Ringneck Pheasant=1135 gm Rased on a rat LD50 of 390 mg/Kg Ringneck LD50=167 mg/Kg

Mammalian Acute RQ<sup>1</sup> (LD50/ft<sup>2</sup>)= 0.0000004

 $^{1}$  RQ = Rate (lbs ai/A) \* (453,590 mg/lbs/43,560 ft<sup>2</sup>/A)x 80% = 65316 mg/43560 = 1.5 mg/sqft LD50 mg/kg \* Weight of Animal (g) \* 1000 g/kg 390 x 100 x 1000 3900000

Avian Acute Oral RQ (Pheasant)=  $\frac{1.5 \text{ mg/sq ft}}{189545000}$  = 0.00000001

The results above indicate that for aerial application of protease bait products at 0.18 lbs ai/A, no mammalian or avian acute levels of concern are exceeded. Currently, EFED has no procedure for assessing chronic risk to mammalian species for protein bait products.

### **Hazard to Non-Target Insects**

Currently, EFED does not quantify risk to nontarget insects. Results of acceptable studies and actual field use observations are used for recommending appropriate label precautions. Acute toxicity to honeybees from acute contact or foliar contact with malathion residues is very high. Based on these acute studies and observations from field studies presented under the previous toxicity to insects section of this document, acute hazard is expected for non-target pollinator insects (honeybees, etc) exposed to direct spray droplets, to residues on foliage, or to residues which are transported on pollen back to the hives or nests (Gary, N.E., 1984). This hazard can extend to pollinators with hives located several kilometers away from the application site, dependent on the distance range of flight paths associated with the particular species in question. Several field studies have shown increased mortality for colonies located as much as two kilometers away from application sites. Many other beneficial species of insects and arachnids (lacewings, butterfly larvae and adults, spiders, beetles etc) are vunerable to non-crop spray applications which are used to control other pests of public concern such as medflies, mosquitoes, and flies (Dahlsten, D.L., 1983; Johansen, C.A., 1965). Spraydrift to aquatic habitats may produce adequate residue levels to prove hazardous to aquatic larvae of insects which later become important terrestrial members of the insect community (eg. dragonflies, mayflies, damselfiles, snipeflies, caddisflies, stoneflies etc.). Mortality to these types of larvae may occur at aquatic concentrations as low as 1 PPB. Studies by L.D. Jenson, 1965 showed that even after stonefly larvae were removed from exposure areas and placed in clean water mortality could still occur within 24 hours. Many of these larvae also serve as important food sources for juvenile fish.

## Risk to Nontarget Freshwater or Estuarine Aquatic Organisms

Based on actual monitored concentrations, predicted modeling results, and actual fish kill incidents, there is acute hazard from contamination of aquatic habitats adjacent to or within target application areas. Tables presented below represent risk quotients for various application scenarios for agricultural and public health uses of malathion. Risk quotients which exceed 0.5 are considered to present acute hazard to the species in question. Risk quotients which exceed 0.05 are considered to offer potential hazard to endangered species within these groups (fish, crustacea, amphibia, etc). The tables below present risk quotients for invertebrates and fish in the same table. The first number in each scenario cell pertains to the RQ associated with the acute EC50 (1 ppb) or chronic NOEC (0.06 ppb) associated with *Daphnia magna*. The second number in the cell represents the RQ for fish based on the LC50 of the bluegill sunfish (30 ppb) or the chronic NOEC for the rainbow trout early life stage test (21 ppb). Though the bluegill was not the most sensitive value in the Fish and Wildlife Service Dataset, it was felt to be most representative of the warmwater habitats associated with the major use areas for malathion. The RQs are derived using predicted EECs from GENEEC (tables 35 and 36) or PRZM/EXAMS (table 37) and dividing them by the acute or chronic toxicity endpoints. Malathion usage involves so many crop uses that Tier II modeling was not possible or practical for all scenarios.

Table 34. Aquatic Organism Acute Risk Quotients-Invertebrate RQ/Fish RQ

Cheminova and IR4 Supported Maximum Tolerance Rates and Crop Scenarios

							Applicat						
	Rate	Int.	1	2	3	4	5	6	7	8	9	10	12- 25
A	0.175	7D	Inv/Fish								8.2/ 0.3		
В	0.50	NA	11.4/0.38										
С	0.61	5D					*						
C		7D		23.2/0.8	27.7/0.8								
C		14D		26.8/0.90									
D	0.76	10D					40.6/1.35						
E	0.94	3D	21.7/0.73										
E		6D						45.4/1.52					
E		7D			42/1.4				42/ 1.4				
F	1.0	7D						45.2/1.52					
G	1.25	3D	28.5/0.92	54.3/1.8				90.4/3.0					91.9/ 3.0
G		5D					66/2.2						
G		7D			56.1/1.8	56.5/1.8	56.5/1.8	57.2/1.9	56.5/ 1.8	56.6/ 1.8	56.6/ 1.8	56.6/ 1.8	
G		14D		47.1/1.58									
Н	1.50	7D			67.3/2.24			67.3/2.24					
I	1.56	7D		67.8/2.24			70.8/2.3						
J	1.88	5D						99.4/3.3					
J		7D			84.4/2.8	84.9/2.8		85/2.8					
J	1.88	14D		70.8/2.8									
K	2.03	6D						98/3.2					
K		7D			91.1/3.0	91.7/3.0							
L	2.5	3D											181/ 6
L		5D			128/4.2								
L		7D			112/3.7		113/3.7						
M	3.43	5D					181/5.9						

N	3.75	7D			169/5.5	169/5.5			
N		14D			142/4.7				
O	4.7 lb	30D	171/5.6						
P	5.0	7D		224/7.4	225/7.4				
Q	6.25	30D		226/7.4					

Table 35. Aquatic Organism Chronic Risk Quotient (Invertebrates RQ/Fish RQ)

(Cheminova and IR4 Supported Max. Tolerance Rates and Scenarios- 0.175 to 6.25 lbs ai/Acre)

				11			of Applic	ations					
	Rate lb ai/A	Int. Day	1	2	3	4	5	6	7	8	9	10	12- 25
A	0.175	7D	inv/fish									33/ 0.04	
В	0.50	NA	46/0.05										
С	0.61	5D		95/0.1	114/0.12								
C		7D		110/0.12									
C		14D											
D	0.76	10D					167/0.16						
E	0.94	3D	167/0.02										
E		6D						187/0.2					
E		7D			173/0.2				175/0.1 9				
F	1.0	7D						187/0.2					
G	1.25	3D	116/0.12	207/0.24				372/0.4					38/ 1.65
G		5D					270/0.3						
G		7D			230/0.25	230/0.25	230/0.25	235/0.26 (Aerial)	230/ 0.25	230/ 0.25	230/ 0.25	230/ 0.25	
G		14D		194/0.3									
Н	1.50	7D			277/0.3			277/0.3					
I	1.56	7D		194/0.3			292/0.31						
J	1.88	5D						410/0.44					
J		7D			347/0.37	350/0.37		350/0.37					

J	1.88	14D	392/0.31							
K	2.03	6D					404/0.43			
K		7D		375/0.4	226/0.4					
L	2.5	3D								746/0 .8
L		5D		527/0.57						
L		7D		462/0.5		465/0.5				
M	3.43	5D				534/0.8				
N	3.75	7D			696/0.75		696/0.75			
N		14D			585/0.63					
O	4.7	30D	704/0.75							
P	5.0	7D		923/1.0	924/1.0					
Q	6.25	30D		931/1.0						

**0.175 lbai/A** A10=Orange, Grapefruit, Lemon, Lime, Tangerine, Tangelo, and Kumquat

**0.50 lb ai/A B1**=Flax

0.61 lb ai/A C5(5D)=Sweet Corn, C2(7D)=Hops, C3(7D)=Beans, Corn, Rice, Sorghum, Wheat, and Rye

C2(14D)=Alfalfa, Clover, Lespedeza, Lupine and Vetch

**0.76 lb ai/A D5**=Blueberry

0.94 lb ai/A E1(3D)=Grass for hay, E4(3D)=Mushroom, E6(6D)=Strawberry, E3(7D) = Peppermint and spearmint,

E7(7D)=Macadamia

1.0 lb ai/A F6(7D)=Melons, Watermelon, Pumpkin and Winter Squash

1.25 lb ai/A G1(3D)=Grass for hay, G2(3D)=Field corn, G2(7D) Brussel sprouts, cauliflower, collards, kale, kohlrabi G6(3D)=Mustards,

 $\begin{array}{l} G25(3D) = \text{Cotton}, \quad G5(5D) = \text{Watercress}, \quad G3(7D) = \text{Rice}, \\ \text{Sorghum}, \quad \text{Wheat}, \\ \text{Rye}, \quad \text{Barley}, \\ \text{Oats} \quad \text{and Corn}, \quad G4(7D) = \\ \text{Blueberry}( \\ \text{ULV}), \quad G5(7D) = \\ \text{Turnip}, \\ \text{Broccoli}, \quad \text{Apple}, \\ \text{Sweet Potato}, \\ \text$ 

G6(7D)= Cabbage and Cherry(ULV), G7(7D)=Carrot, G8(7D)=Mango and Passion fruit, G9(7D)=Asparagus G10(7D)=Pears and Quince, G12(7D)=Guava and Papaya, G2(14D)=Alfalfa, Clover, Lupine, Vetch and Lespedenza

**1.5 lbs ai/A H2(7D)**=Celery, **H6(7D)**=Okra

1.56lbs ai/A I2(7D)=Potato, Sweet potato, I5(7D)=Onion, Garlic, Shallot, Leeks

1.88 lb ai/A J6(5D)=Lettuce, J4(7D)=Blackberry, Raspberry, Loganberry, Boysenberry, Dewberry, Currant, Gooseberry,

J3(7D)=Cucumber, Chayote, J6(7D)= Strawberry, J2(14D)=Grapes

2.03 lbs ai/A K6(6D)=Strawberry(50%WP), K3(7D)= Spinach, Dandelion, Endive, Parsley and Swiss Chard,

**K4(7D)**=Blackberry, Raspberry, Gooseberry, Loganberry, Dewberry, Currant and Boysenberry

2.50 lb ai/A L25(3D)=Cotton, L3(5D)=Figs, L3(7D)=Mustards, Walnuts, and Pecans, L5(7D)=Peas

3.43 lb ai/A M5(5D)=Tomato, Pepper, Eggplant

3.75 lb ai/A N4(7D)=Apricots, N6(7D)=Cherry, N4(14D)=Peach and Nectarine

4.7 lb ai/A O2(30D)=Avocado

5.0 lb ai/A P3(7D)=Pineapple, P4(7D)=Chestnuts

**6.25 lb ai/A** Q3(30**D**)=Oranges, Grapefruit, Lemon, Lime, Tangerine and Tangelo

## Table 36.

# PRZM-EXAMS Derived Aquatic RQ's

(EECs Based on 1 in 10 Year Events)

						ľ	Model R	esults (ppb)		
	% of total a.i.	Use rate	Interval	No. of	PRZ	ZM-EX	AMS	Acute/Chronic RQ's		
Crop	applied / year <sup>1</sup>	(lbs a.i./A)	(days)	applications	peak <sup>2</sup>	21d ave	60 d ave. <sup>3</sup>	Inv.	Fish	
~		Max: 2.5	3	25	291	67.4	47.7	291/674	9.7/2.3	
Cotton	41.6%	Typ: 0.3	[3] <sup>4</sup>	4	7.9	1.48	0.50	8/15	0.26/0.02	
416.16	22.5%	Max: 1.25	14	2						
Alfalfa	Alfalfa 23.5%	Typ: 1.4	[14]	1						
G 1	7.40/	Max: 1.25	7	3	26.7	5.01	1.95	27/50	0.9/0.09	
Sorghu m	7.4%	Typ: 0.8	[7]	1	2.94	0.50	0.18	3/5	0.09/0.01	
		Max: 1.25	7	5	0.80	0.33	0.19	0.8/3	0.03/0.01	
Apple	2.14%	Typ: 0.7	[7]	3	0.59	0.24	0.09	0.59/2	0.02/0.004	
		Max: 6.25	30	3	162	25.2	11.1	162/252	5.4/0.5	
Citrus	0.49%	Typ <sup>5</sup> : 2.5	[30]	1	47.3	7.38	2.59	48/74	1.57/0.12	
	0.45-	Max: 1.88	5	6	15.4	6.26	2.98	15/63	0.5/0.14	
Lettuce	0.45%	Typ: 2.0	[5]	1	5.63	1.58	0.56	6/16	0.18/0.02	

## PRZM EXAM Runs Correspond to the Following Use Scenario Numbers:

1.25 lb ai/A G3(7D)=Rice, Sorghum, Wheat, Rye, Barley, Oats and Corn, G5(7D)=Turnip, Broccoli,

Apple, Sweet Corn, Beet, Chayote, Horseradish, Parsnip, Radish, Rutabaga, Salsify, Sweet potato,

G2(14D)=Alfalfa, Clover, Lupine, Vetch and Lespedeza

1.88 lb ai/A J6(5D)=Lettuce 2.50 lb ai/A L25(3D)=Cotton

**6.25 lb ai/A Q3(30D)**=Oranges, Grapefruit, Lemon, Lime, Tangerine and Tangelo

Table 37. MALATHION NON AGRICULTURAL USE-Maximum Labeled Rates High Exposure Scenario EECs and RQs Direct Application to Water or 100% Drift\*

USE LOCATION (Predicted U.S. Acreage)	Max. Rate lbs ai/A	Max # Applic.	Min Int	Acute Aquatic EEC s 0.5-6 ft in ppb	Acute Aquatic Risk Quotient
Nonagricultural rights of way/fencerows/hedgerows (17,000 acres)	0.598	NS	NS	438 to 36	Inv438 to 36 Fish-14 to 1.1
Mosquito Control (8,227,000 acres) Lakes/Ponds/Reservoirs(human use)(0.5985) Nonag. Uncultivated Areas/Soils (0.6) Polluted Water (0.6)	0.630 ULV Aerial	NS	NS	462 to 38	Inv462 to 38 Fish-14 to 1.2
Lakes/Ponds/Reservoirs (No Human Use) (0.628) Swamps/Marshes/Wetlands/Stagnant Water (0.628) Intermittently Flooded Areas/Water (0.628)	0.630 Ground Fogger	NS	NS	92.4 to 7.6 (20% drift)*	Inv92 to 8 Fish-2.9 to 0.25
Woodland Use (17,000 acres) Pine Forest/Shelterbelt (0.9375) Eastern White Pine (Forest) (0.9375)	0.94	NS	NS	688 to 57	Inv.=688 to 57 Fish=21 to 1.7
Rangelands/Pastures/Set Aside Acreage/Summer Fallow (1,625,000 acres) Canarygrass (1.2) Rangeland or Pastures (1.25) Grass Forage/Fodder/Hay (1.25)	1.25	NS	NS	917 to 76	Inv.=917 to 76 Fish=29 to 2.4
Ornamental Plant Uses-Nurseries-Homeowner (175,000 acres) Ornamental trees and Herbaceous Plants	1.746	NS	NS	direct drift unlikely	Not computed
Ornamental Nonflowering Plants Ornamental Woody Shrubs and Vines (2.5)	2.50	NS	NS	direct drift unlikely	Not computed
Commercial Tree Production (no est. acreage) Christmas Tree Plantations, (3.125) Ornamental and/or Shade Trees (3.125) Slash Pine (forest) (3.125)	3.125	NS	NS	2293 to 190	Inv.=2293 to 190 Fish=72 to 6.0
Public Parks (67,000 acres)	NS			Rates not specified	Not computed
Turf Use/ Golfcourses/Commercial Lawncare Ornamental Lawns and Turf	5.1	NS	NS	direct drift unlikely	Not computed
No Non-Ag uses at higher rates (>5.1 lb ai/A)	Not supported				Not supported

NS=Not Specified

NS=Not Specified

\*Drift from truck mounted foggers is not expected to exceed 20% deposition due to continuous drift of micro droplets on air currents.

<sup>\*</sup>Drift from truck mounted foggers is not expected to exceed 20% deposition due to continuous drift of micro droplets on air currents.

## **Endangered Species**

Endangered species LOCs are exceeded for malathion for acute hazard to endangered fish, aquatic invertebrates (with possible exception of molluscs), and insects for most outdoor uses. Chronic hazard LOC's to threatened birds, mammals, amphibians and reptiles are potentially exceeded for certain uses. Chronic hazard LOC's for endangered fish and invertebrates are exceeded by most uses. The magnitude of malathion use and the numbers of potentially exposed endangered species will require more extensive analysis by the OPP Endangered Species Branch.

The Endangered Species Protection Program is expected to become final in the future. Limitations in the use of malathion will be required to protect endangered and threatened species, but these limitations have not been defined and may be formulation specific. EPA anticipates that a consultation with the U.S. Fish and Wildlife Service will be conducted in accordance with the species-based priority approach described in the Program. After completion of consultation, registrants will be informed if any required label modifications are necessary. Such modifications would most likely consist of the generic label statement referring pesticide users to use limitations contained in county Bulletins.

# **Risk and Exposure Characterization**

The following section identifies major routes of exposure expected to lead to effects on ecological resources and the highest exposure levels for drinking water sources. These are direct aerial applications to large areas, spray drift, and runoff in nonagricultural settings. The use patterns of highest Agency concern are those expected to cause the highest off-target EECs of malathion and malaoxon.

#### Summary of Expected Paths of Potential Exposure for Wildlife

### Direct Application Public Health Use

Aerial and ground spray applications of malathion allow for coverage of large areas of urban, suburban, and rural areas. For instance malathion may be applied aerially "...over cities, towns, and other areas..." (Fyfanon ULV Insecticide label) for adult mosquito control. Rates of malathion use for mosquito control are permitted at up to 9.9 lbs ai / mi² / year in the following states: Washington, Oregon, Utah, Wyoming, Texas, Louisiana, Mississippi, Michigan, Alabama, Florida, Georgia, South Carolina, North Carolina, New Jersey, and Virginia. In some areas urban and agricultural use of malathion may overlap. Terrestrial wildlife, insect, and adult amphibian exposure from this type of use is expected to be through a multitude of food sources receiving residue including vegetative food matter, insects, drinking water and also through direct dermal and inhalation exposure to spray applications. Aquatic exposure to fish, crustacea, mollusca, arthropoda, and larval amphibia is expected to be primarily from drift with lesser amounts contributed by runoff.

Malathion for adult mosquito control is applied by fogging and aerial methods at relatively low rates. Thermal aerosols or fogs create very small droplets of malathion (<20μm) that can be carried on air currents for long distances before contacting plants, water, or soil. Because of this tendency, malathion in fogs is expected to dissipate largely through atmospheric diffusion with relatively little deposition onto water or soil. Wang *et al* (1987) studying fenthion fog deposition on water measured 5-6% deposition of the applied insecticide. EFED has used a more conservative estimate of 20%. For aerially applied ULV formulations higher deposition is expected because droplet size is larger (up to 100μm) and there are no specified protective buffer zones. Thus, it is assumed by EFED that 100% deposition occurs in shoreline areas and decreases as the fog spreads across the water surface.. Based on low toxicity thresholds of 0.5 ppb (invertebrates) to 10 ppb (fish), 20% to 100% drift scenarios, actual monitored residue levels and observed adverse effects in actual use situations risk quotients for aquatic invertebrates and fish are expected to be exceeded in shallow littoral zones.

In areas close to the fogging apparatus or beneath aerial applications inhalation may be a potential route of acute exposure for terrestrial wildlife. Mammalian toxicity data provided to HED show severe effects to rats in the lowest exposure group of 0.1 mg/l (96 h). The no effect level is not defined and it is not known what interspecies differences in sensitivity exist. Although it is not clear what atmospheric malathion concentrations are acceptable, the levels generated during mosquito control are expected to be very transient. Direct exposure to flying non-target insects is not only likely, but probably unavoidable as fogging type applications are designed to contact flying insects.

### Ground and Airblast Application to Agricultural Sites

Normal malathion ground application usage in agricultural field settings presents potential chronic risks for terrestrial wildlife, but lower risk to aquatic life than aerial applications. Key issues identified are possible chronic effects resulting from repeated 3 to 7 day pulse exposure of birds to malathion at certain rates of application, increased risk to wildlife resulting from exposure to malathion products containing mixtures of other insecticides and fungicides, and direct contact toxicity to beneficial insects from off target drift from agricultural target areas or later contact with residual malathion residues on the target crops. Some toxic exposure to aquatic organisms from small amounts of runoff is expected, though exposure from spraydrift will be less than for aerial application.

Synergistic toxicity resulting from co-exposure to malathion and other pesticides has been noted in previous portions of this review. Not only are malathion mixtures with other pesticides marketed as end-use products, but agricultural use of malathion is commonly accompanied by the use of other pesticides in the same field leading to mixtures of residues in the field. Runoff and drift of malathion also mixes with residues of many other pesticides used in fields adjacent and in the same drainage basin. Some cholinesterase inhibiting insecticides are expected to result in additive toxicity when combined with malathion, although some other pesticides have been shown to potentiate malathion toxicity. Greater than expected toxicity has been noted when combined with certain cholinesterase inhibiting insecticides (including carbaryl and EPN) and some fungicides (including clotrimazole). The environmental and ecological effects of mixtures is poorly understood, but in many instances, increased sensitivity of organisms is expected. More data concerning the toxicities of these end-use product mixtures as well as mixture with other pesticides in normal agricultural use is needed to assess these concerns for malathion.

### Spray Drift from Agricultural Uses

Monitoring results show that spray drift can be a major source of aquatic contamination. Drifting malathion applications carried by air movement will reach unintended sites. More than half of the malathion usage in the United States is applied in ULV formulations which are highly prone to drift when applied aerially. ULV formulations are popular with aerial applicators because they are very concentrated and allow the treatment of large acreage without returning to the airfield for refilling or refueling.

An assessment of drift as a result of malathion use methods for the Boll Weevil Eradication Program (presently 60% of all malathion use in U.S.) was conducted by measuring off-target drift adjacent to aerial ULV malathion applications (Penn State 1993). Application conditions were the same as those used in the eradication program. The spray system was a conventional boom and nozzle system fitted with Spraying Systems stainless steel 8002 Flat Fan spray tips. The nozzle position was straight down and the flying height was a nominal 5 feet above the crop canopy. Drift was measured from single aircraft passes delivering 1 lb/A. Wind direction was perpendicular to the flight path. Seventeen runs were conducted under varying meteorological conditions. Maximum depositions were 21, 12, 2.8, and 0.7% of the expected maximum at 100, 200, 300, and 1000m downwind (Penn State 1993). The highest amount of drift at 1 km occurred when atmospheric conditions were stable, meaning vertical air mass movements are dampened. Higher drift levels at shorter distances occurred under unstable, windy conditions. Averages of results under different atmospheric conditions show deposition of 9.4% at 100 m while at 1000m the deposition rate was 0.08%.

Using deposition rates from the Penn State study it is possible to calculate aquatic EECs for varying depths of water based on direct application of the expected % of drift and using a 6 inch to 6 foot depth range for the standard 1 acre farm pond scenario.

	Table 38. Maximum downwind drift aquatic EECs and risk quotients									
water	( ,				(12% depo	osition)	300 m (2.8% deposition)			
depth (in)	EEC	RQ (fish)	RQ (daphnia)	EEC	RQ (fish)	RQ (daphnia)	EEC	RQ (fish)	RQ (daphnia)	
6	154	5.1	154	88	2.9	88	20.5	0.68	20.5	
72	25.6	0.85	25.6	7.3	0.24	7.3	1.7	0.06	1.7	

Based 1 lb/acre (used in the Penn State drift study) drifting to a one hectare pond. Risk quotients are based on fish LC50 for bluegill (30 ppb) and *Daphnia magna* LC50 (1 ppb). The effects of reducing spray drift was examined two ways: first, varying the drift parameters in PRZM-EXAMS modeling and, second, by comparing the effect different application practices and buffer strips on measured drift in monitoring studies.

Levels of concern for fish are exceeded at 100 and 200 m distances with these maximum drift values. At 300 m a level of safety is achieved for fish, but daphnids are still at risk. Monitored values of malathion drift to streams suggest that table above is conservative in estimating aquatic risk. A typical range of monitored values is shown in Table 13a ranging from non-detected to almost 11 ppb 25 feet from the field. In these applications wind direction was away from the water.

The Boll Weevil Eradication Program mostly uses ultra low volume (ULV) formulations in its program in several states. ULV which is ~95% malathion is the most cost effective formulation in the treatment of cotton for boll weevil because it is concentrated and enables aerial applicators to treat large areas before refueling and refilling. ULV applications results in the formation of small droplets of the pesticide which are prone to drift long distances. The speed by which droplets fall is exponentially dependent upon their size such that small droplets fall very slowly. Smaller droplets result in more non-target deposition of pesticide through drift caused by wind, thermal air currents, and turbulence from applicator planes. Presently at least 14 different crops receive aerial ULV applications of malathion. These crops include alfalfa, blueberries, clover, cotton, dry beans, corn, sorghum, grass, lima beans, oranges, rice, snap beans, wheat, and cherries. Drift from non-ULV formulations is significantly lower under analogous application conditions.

Monitoring studies suggest that reducing drift dramatically reduces aquatic EECs. Boll weevil treatments were examined for drift to surface water in the Southeast and Texas. Table 12a shows the effects of ground versus aerial application and varying buffer strips on malathion drift by measuring concentrations before and at 15 minute increments after application. Four different sites are examined with buffer strips ranging from 700 feet with 30-60 foot trees to 25 feet with lowlying vegetation. Five other sites shown in previous tables related to actual field monitoring results provide additional information on drift but lack site and application information which led to the monitored residue levels.

Monitoring data suggests that wider buffer strips and ground applications reduce drift. Aerial applications to two fields with 125 foot or greater buffers resulted in no measured drift. Aerial applications to a 95.3 acre field with a 100 foot buffer containing mature hardwoods (Pursley Creek site) resulted in minor drift: only three measurements of six total were greater than 3 ppb above background. Four aerial applications to a 19.2 acre field with a 25 foot buffer containing low kudzu vegetation (Stewart Creek) resulted in significant drift: all four events resulted in aquatic concentration exceeding 3 ppb. Five ground applications to the same site resulted in low drift: four of five ground applications resulted in aquatic concentration of less than 0.33 ppb.

### Runoff in Urban Scenarios

Though initial exposure of non-target aquatic habitats is expected to be primarily through spray drift, monitored residue levels in residential storm water runoff events have yielded high residue levels, despite the short terrestrial half-life values that are reported for malathion.

It should be noted that monitored runoff events in urban areas reflect aggregate malathion residues resulting from all uses of malathion in that particular drainage basin such as homeowner use, commercial turf use, municipal mosquito control use, and commercial agricultural use. There are approximately 60 home and garden products containing malathion and malathion/methoxychlor on the market.

Monitoring data of runoff from urban-use sites is frequently high probably due to increased runoff from impermeable surfaces and increased persistence on microbially inactive, dry surfaces. The fastest routes of malathion degradation are through aerobic metabolism and hydrolysis. Residential surfaces such as asphalt and concrete, which malathion is likely to contact in urban use, do not provide microbes and moisture required for these degradation pathways. A CalEPA study and monitoring data also suggest that the toxic degradate malaoxon is more likely to form on residential surfaces and occur more frequently in urban runoff. Anthropogenic surfaces are less likely to retain malathion during rainfall which would lead to pulses of malathion in storm water runoff which drain into urban streams. USGS NAQWA data show higher levels of malathion and more detects in urban streams than were monitored in rural and agricultural counterparts. In medfly control efforts south of San Francisco in 1984 residue levels increased significantly after rainfall events. Fish kills coincided with high levels of malathion (80-800 ppb) after rainfalls. Application rates and methods for mosquito control and medfly programs are similar, thus runoff resulting from urban mosquito control operations may be similar to those observed from medfly applications. Malathion is used in community mosquito control programs in at least 15 states up to 9.9 lbs / mi<sup>2</sup> / year. This assessment indicates that risk to aquatic life from runoff transported residues will be high in urban use scenarios.

#### Runoff in Agricultural Scenarios

Agricultural field runoff of malathion to nontarget aquatic habitats has been observed to be generally low, probably due to rapid degradation on soil. Runoff monitored in the Boll Weevil Eradication Program suggests that a majority of malathion levels in receiving waters will not present a significant risk for fish. The risk level for invertebrates from runoff is less clear. Malathion in runoff from cotton fields ranged from none detected to 146 ppb in undiluted drainage. Dilution of runoff and therefore the degree of risk for invertebrates will vary with the size of the body of receiving water. A dilution factor of nearly 300 is necessary to reduce the daphnid RQ to below 0.5. This would be expected in larger receiving water bodies but agricultural field runoff to small streams and ponds will result in higher risk.

### Malathion Non-Crop Usage in Rural Scenarios

Malathion is used in a variety of settings which are rural in nature, but not related to a particular crop. Malathion ULV uses include aerial and ground application to control grasshopper and beet leafhopper on pasture lands, rangeland, "non-agricultural" lands(wasteland and roadsides), fencerows, feed-lots, clover(usually a cover crop) and summer fallow. In addition malathion ULV labels list woodland uses via aerial application to control forest insects on douglas fir, true fir, spruce, hemlock, pine, and larch trees to control budworms, looper, sawfly, spittlebug and larch casebearer. Registrants have stated an intention to remove forest uses, but this may not apply to privately owned wood lots and wooded lands. These use patterns are similar to mosquito control scenarios in that they are not directed at any particular field site, yet labeling language does not include specific instructions to aid in protection of sensitive aquatic habitats contained within these areas nor do they specify maximum seasonal application restrictions. They are also similar to agricultural sites in that soil degradation is likely to be more pronounced than in urban scenarios. The total acreage of these types of use sites will total over 2 million acres on a yearly basis.

Exposure risk to avian and mammalian species from repeated applications with narrow intervals is therefore concluded to exist for these use scenarios. Exposure risk from runoff is likely to be equivalent to or perhaps less than agricultural crop sites which presumably might have more bare soil surfaces. Danger of off target drift and to some extent runoff (grasslands) to aquatic habitats may be reduced by foliar intercept in some cases. However, without precautions such as buffer zones to protect bogs, potholes, streams, marshes and other aquatic habitats common to these areas it is assumed that direct drift contamination to these habitats may occur with detrimental effects to aquatic vertebrates and invertebrates. Protection of beneficial or endangered insects with such applications would appear to be impossible. It is therefore assumed that acute risk to non-target insects will occur.

## Spatial Distribution of Potentially Effected Habitats and Species Groups

### Terrestrial Wildlife Utilization of Major Malathion Usage Areas

The following summary of potential major exposure areas for malathion usage is based on EPA Quantitative Usage Analysis data prepared in 1997. Maximum usage estimates were used to allow for potential shifts in market usage of malathion products. Species expected in various crop scenarios were drawn form Wildlife Utilization of Croplands, Gusey, William F. And Z. Maturgo, 1973. The purpose of this portion of the document is not to categorize every species type that could conceivably be exposed to the vast number of potential malathion use sites, but instead to provide a general overview of the species types which might be present for crop and non-crop use sites and to categorize which areas of the country (where possible to predict) may be most heavily impacted by the type of use pattern. Aquatic species are too numerous to list so habitat types common to use sites were listed instead.

Table 39. Terrestrial Wildlife Utilization of Major Malathion Usage Areas

Crop Group	Maximum Usage(acres)	Major States for Malathion Usage	Species Common to Usage Locations
Berry Crops (Blueberry, blackberry, strawberry, etc)	70,000	OR, MI, NJ, WA, CA	waterfowl, quail, pheasant, crows, blackbirds, songbirds(finches, robins, starlings, cedar waxwing), grouse, rabbits, deer, racoon, woodchuck, skunk, opossum,
Citrus Crops	14,000	FL, CA, AZ	doves, roadrunner, screech and horned owls, hummingbirds, gilded flicker, laderbacked woodpecker, western kingbird, verdin, cactus wren, mockingbird, thrashers, orioles, cardinals, grosbeaks, goldfinch, linnet, deer, raccoon
Pome Fruits(apple, pear), Avocado, Figs, Grapes	102,000	WA, MO, MI, TX, GA, CO, CA, TN, FL, MS, OH, AZ	grouse, pheasant, songbirds(bluebird, cardinal, catbird, flicker, blue jay, kingbird, magpie, mockingbird, phainopepla, robin, fox sparrow, thrashers, thrushes, vireos, cedar waxwing, woodpeckers), hawks, bear, fox, marmot, porcupine, rabbit, deer, quail, flicker, racoon, opossum, partridge
Stonefruits (apricots, cherries, peach, nectarine)	64,000	OR, WA, GA, TX, AL, MS, MO, CA, AZ	doves, songbirds(blackbirds, grosbeaks, cedar waxwings, robins, starlings western tanager, brown thrasher, titmouse, orioles, jays, finches, etc), pheasant, wild turkey, rabbit, deer, fox, opossum, raccoon, squirrel,
Nut Trees	57,000	CA, TX, LA, GA, OK	
Bulb vegetables (onion, garlic, etc)	37,000	CA, UT, MI, ID, GA	pheasant, rabbit, deer, songbirds, dove
Leafy, Legume, Tuber and Root, Fruiting, Cucurbit and Other Vegetables	315,000	CA, TX, AL, MI, FL, OH, NY, IL, AZ, MS, MO, MN, WI, ID, IN, WA, OR, VA, NC, WV, UT, NJ, GA	turkey, California, scaled, valley, and bobwhite quails, songbirds(buntings, larks, pidgeon, sparrows, roadrunner, grosbeak, ground doves, pipits), shorebirds, coots, ducks, geese,crows, doves, sandhill crane, prairie chicken, partridge, owls and hawks(feeding on field rodents), coyote, muskrat, gray squirrel, groundhog, elk, skunk, rabbits, raccoon, opossum, woodchuck, deer,
Cereal Grain Crops (barley, corn, rice, wheat, sorghum, oats, rye, rice)	697,000	GA, CO, TX, AZ, KY, VA, MN, MT, NC, ND, CA, NY, NC, PA, TX, AR, MS, LA, KS, MO, NE, SD, TN, OK,	rabbits, pheasant, pigeon, doves, ducks( black, canvasback, mallard, pintail, ringnecked, shoveler, teal, wood), coots, rails, egrets, herons, ibis, and gallinules(rice fields), geese, swan, songbirds( blackbirds, towhees, thrasher, sparrows, junco, magpie, snow buntings, grosbeaks, jays, cardinal, bobolink, meadow and horned lark),woodpeckers (eat seeds), ravens, grackles, crows, partridge, grouse, scaled and bobwhite quail, sandhill crane, Attwater prairie chicken(TX), deer, elk, antelope, wild turkeys, gray, fox and ground squirrel, woodchuck, fox, porcupine, coyote, moles, whitefooted and pocket mice, kangaroo rat, muskrat, javelina(TX)

Cotton + USDA Bollweevil	796,000	TX	deer, turkey, squirrel, rabbit, quail, dove, pheasant, prairie chicken, raccoon, oppossum, sandhill crane, antelope
Grass and Non-grass Forage Crops (alfalfa, clover, hay)	605,000	CA, ID, MT, OK, AZ, KS, TX, MO, SD, KY	pheasant, mourning dove, partridge, quails, ducks, Canada geese, elk, deer, antelope, grouses, prairie chickens, rabbits, turkey, songbirds, cranes, skunk, small mammals, marmot, ground squirrels,
Hops		OR, WA	pheasant, quail, songbirds, doves, owls and hawks feeding on small mammals
Mint	31,000	IN, WI, OR, WA(90%)	pheasant, quail, doves, songbirds, partridge
Pasture lands	47,000	LA, MO, FL, GA, TX, MS	field and vesper sparrows, bobolink, meadow and horned lark, goldfinch, swallows, pipit, cowbird, red polls, juncos, longspurs, blackbirds, crows, nighthawk, whippoorwill, yellow, palm and prairie warblers, grackles, flickers, bluebirds, and indigo bunting.
Private Lots/Farmsteads	66,000	FL, CA, SD, AL, OK, KS (60%?)	No definitive state surveys were reviewed.
Set Aside Acreage	665,000	MT, MN =(90%?)	No definitive state surveys were reviewed
Summer Fallow	893,000	MT, TX = (100%)	No definitive state surveys were reviewed
Rangeland	20,000	TX, FL, CO =(85%)	No definitive state surveys were reviewed
Woodlands	17,000	AL, LA, TN=(81%)	No definitive state surveys were reviewed
NON Agricultural			
Roadways and fencerows	17,000	Nationwide	sparrows, kingbirds, flycatchers, yellowbreasted chat, indigo bunting, bluebird, goldfinch, brown thrasher, catbird, robin, woodpeckers, yellow and palm warblers, and vireos.
Golf Courses	>12,000	Nationwide	Waterfowl including snow and Canada geese (may feed on treated turf), squirrels and other small mammals(in rough areas), ground feeding songbirds, ie robins,
Nurseries	175,000	Nationwide	
Parks	67,000	Nationwide	Many types of songbirds, small and large mammals,
Landscape Contractors- Bldg Perimeters/Grounds	No estimates	Nationwide-Urban	Songbirds
Cemeteries	21,000	Nationwide -Urban	Same as parks

Mosquito Control	8,227,000	Nationwide near population centers, particularly those surrounded by static aquatic settings ie beach resorts, lake shore communities, low water or flood prone areas	Saltmarshes: Bank and tree swallow, fish and common crow, savanna, seaside, and Sharp tailed sparrowl, redwing blackbird, horned lark, egrets, rails, shorebirds, gulls, herons, gallinules, other waterfowl, muskrat, otter,  Freshwater marshes and wet woodlands: marsh, winter and Carolina wrens, swamp, Savanna, sharp-tailed sparrows, swallows, water thrush, ovenbird, phoebe, wood pewee, veery, bluegray gnatcatcher, yellow breasted chat, warblers(hooded, yellowthroat, blackcapped, and Wilson's), racoon, muskrat, beaver,
Proposed for Revocation of Uses Soybean, Peanut, Sunflower	226,000	GA, OK, NC, FL, TX, TN, MN, MO, IN, AR, KS, SD, ND	Species groups not categorized due to impending revocation of use on these crops

### Aquatic Organisms: Utilization of Habitats Exposed to Malathion Usage

Numerous types of agricultural uses of malathion may border valuable aquatic habitats such as streams, rivers, lakes, and freshwater marshes. Many of these tributaries may drain to estuarine areas. A few of the crop uses may actually involve sites which border estuarine areas (ie citrus). In some cases, irrigation canals near crop sites will contain fish and shrimp populations and also drain to natural water sources. In general, malathion incidents have involved pulse loading of malathion to streams and ponds following heavy rainfall events or aerial spraydrift of residues directly to the surface of standing water bodies. Residue detection in sediments has been rare. In urban scenarios, storm water runoff has provided a point-source type of residue contribution to streams which drain these areas. Malathion poisonings of aquatic organisms are most likely to occur in the early hours of the exposure period immediately after rainfall or spray applications to specific sites. The numbers of species potentially effected is large and the types of habitat exposures quite varied. The following table provides a very general overview of the types of aquatic habitats that are expected to be exposed from various uses of malathion.

Table 40. Aquatic Habitats - Use Associations				
Crop Group	Maximum Use(acres)	Major States for Malathion Usage	Habitats Common to Usage Locations	
Berry Crops (Blueberry, blackberry, strawberry, etc)	70,000	OR,MI,NJ,WA,CA	FW Marshes, ponds, and streams:	
Citrus Crops	14,000	FL, CA, AZ	Irrigation canals, rivers, freshwater springs, some estuaries	
Pome Fruits(apple, pear), Avocado, Figs, Grapes	102,000	WA, MO, MI, TX, GA, CO, CA, TN, FL, MS, OH, AZ	FW streams, rivers, ponds, marshes, and lakeshore	
Stonefruits (apricots, cherries, peach, nectarine)	64,000	OR, WA, GA, TX, AL, MS, MO, CA, AZ	FW streams, rivers, ponds and marshes	

Nut Trees	57,000	CA, TX, LA, GA, OK	Streams, irrigation canals, and rivers
Bulb vegetables (onion, garlic, etc)	37,000	CA, UT, MI, ID, GA	Streams, rivers, bogs
Leafy, Legume, Tuber and Root, Fruiting, Cucurbit and Other Vegetables	315,000	CA, TX, AL, MI, FL, OH, NY, IL, AZ, MS, MO, MN, WI, ID, IN, WA, OR, VA, NC, WV, UT, NJ, GA	Irrigation canals, streams, rivers, bogs, marshes
Cereal Grain Crops (barley, corn, rice, wheat, sorghum, oats, rye, rice)	697,000	GA, CO, TX, AZ, KY, VA, MN, MT, NC, ND, CA, NY, NC, PA, TX, AR, MS, LA, KS, MO, NE, SD, TN, OK,	Streams, rivers, ponds, prairie potholes, marshes, saltmarshes, estuarine bays
Cotton + USDA Bollweevil	796,000	TX	Rivers, streams, possibly marshes
Grass and Non-grass Forage Crops (alfalfa, clover, hay)	605,000	CA, ID, MT, OK, AZ, KS, TX, MO, SD, KY	Ponds, bogs, marshes, streams, prairie potholes
Hops		OR, WA	rivers and streams
Mint	31,000	IN, WI, OR, WA(90%)	Streams
Pasture lands	47,000	LA, MO, FL, GA, TX, MS	Streams, rivers, ponds, prairie potholes, marshes, swamps
Private Lots/Farmsteads	66,000	FL, CA, SD, AL, OK, KS (60%?)	Streams, ponds, bogs, potholes, FW springs
Set Aside Acreage	665,000	MT, MN =(90%?)	Streams, ponds, lakes, marshes and potholes
Summer Fallow	893,000	MT, TX = (100%)	Streams, rivers, and potholes
Rangeland	20,000	TX, FL, CO =(85%)	Streams, rivers, swamps, FW springs
Woodlands	17,000	AL, LA, TN =(81%)	Streams, bogs, rivers, wooded wetlands
NON Agricultural			
Roadways and fencerows	17,000	Nationwide	Drainage ditches, crossing or adjacent streams and rivers, swamps, saltmarshes, ponds
Golf Courses	>12,000	Nationwide	Ponds, streams, marshes, some saltmarsh areas
Nurseries	175,000	Nationwide	Ponds, drainage areas to streams
Parks	67,000	Nationwide	Streams, ponds, and lakes(inland), saltmarshes and ocean shorelines(coastal)

Landscape Contractors- Bldg Perimeters/Grounds	No estimates	Nationwide-Urban areas	Retention and natural ponds, streams, drainage from storm sewers to tributaries
Cemeteries	21,000	Nationwide-Urban areas	Ponds and streams
Mosquito Control	8,227,000	Nationwide near population centers, particularly those surrounded by static aquatic settings ie beach resorts, lake shore communities, low water or flood prone areas	Saltmarsh mosquito control- saltmarshes, estuarine bays, mangrove swamps, shoreline areas  Freshwater mosquito control: freshwater marshes, bogs, and wet woodlands:(Inland areas near population centers
Proposed for Revocation of Uses Soybean, Peanut, Sunflower	226,000	GA, OK, NC, FL, TX, TN, MN, MO, IN, AR, KS, SD, ND	

## **Adequacy of Malathion Toxicity Data**

The toxicological data, though extensive for malathion, is not complete in several key areas. In addition, much of the data is over twenty years old, and, to some extent, was not conducted in accordance with stricter standards which are required of studies presently submitted to support registration of pesticides. One example would be the fact that most of the acute toxicity endpoints for aquatic organisms are based on nominal concentrations which, due to malathion's short aquatic persistence, may not be appropriate since this could lead to calculated LC50 values which are higher than would have been estimated if based on mean measured concentrations.

There are also some other areas where the data set is weak. In formulation testing only one presently employed product formulation (57% EC) was tested on 4 species (daphnid, oyster, honeybee, and sheepshead minnow). There are no submitted toxicity data on the mixture of malathion and methoxychlor, a possibly highly lethal cocktail for aquatic life. There are no studies regarding the chronic effect levels of malathion to estuarine fish or invertebrates which could conceivably be exposed to repeated pulse load exposures for such uses as citrus and cotton. Further data to elucidate potential effects to non-target insect populations is needed. Acute studies with honeybees indicate that acute contact with direct or latent residues may prove lethal for several days after application. Other beneficial insect populations may also suffer acute losses. There is some indication that amphibian life cycles could be effected by malathion exposure. Though not presently a data requirement requested by the Agency, but given what is known about acute and chronic effect levels observed in frogs, a better understanding of effects to this taxa is needed to improve this assessment.

Sublethal effects caused by temporary disruption of nervous system functions are difficult to use in present risk assessment procedures, because so little is known about their ultimate effect on non-target species populations. However, malathion has been shown to disrupt nesting success in sharp tailed grouse, loss of ability of laboratory mice to navigate a maze, and loss of swimming ability for fish swimming against a current. All of these effects theoretically could lead to reduced survival of certain species groups, when combined with the normal stress factors associated with survival (eg. successful rearing of young, escape from predators, and navigation to spawning grounds).

#### **Limitations of Monitored Effects**

Though a large number of incidents associated with adverse effects to aquatic vertebrates near malathion use sites have been reported, very little information regarding effects to invertebrate populations in the same sites was provided. Given the lower toxicity thresholds for invertebrates exposed to malathion, it is expected that lethal effects to these populations are now occurring from present uses, but, due to the difficulty in observing these effects, go unreported. Many of the monitored residue levels in aquatic habitats near malathion use sites have far exceeded 0.5 ppb which is considered a toxicity threshold for acute effects to aquatic invertebrates. Chronic effects were observed in laboratory studies on daphnids at concentrations which are considered the limitation of detection in field monitoring studies (0.1 ppb). Another consideration is that many of the adverse effects reported for malathion are not investigated within the first 48 hours of exposure, thus allowing substantial degradation of the initial peak concentrations which caused the acute reaction observed in the effected organisms.

## **Characterization of Predicted Effects to Nontarget Species from Malathion**

## **Ecological Risk to Birds and Mammals**

Based on estimated risk quotients for dietary exposure scenarios malathion is not expected to offer significant acute hazard to birds even at the proposed maximum application scenarios of 6.25 lbs ai/acre on citrus.

Sublethal effects to birds (reduced AChE levels) may result from exposure to malathion residues. The effects may not in themselves prove lethal, but the ultimate result may prove detrimental to survival when exposed birds are subjected to other stress factors in the environment. When radiotagged sharp-tailed grouse were sublethally dosed with dieldrin or malathion and released back into the wild significant reductions in ability to nest, reproduce and possibly escape predators were observed up to 12 days after dosing (McEwen and Brown, 1966). Control birds all survived and reproduced successfully. In field exposures of birds to malathion applications singing activity was reduced or ceased for up to 2 days following the application.

Chronic exposure for birds presents another matter. In general, malathion is not deemed to be a persistent compound. However, because of the fact that there are no clear restrictions on most of the present labels regarding numbers of consecutive applications, intervals, or avoidance of nesting birds it is conceivable that birds may be subjected to repeated peak levels within very short time intervals. Regressed ovaries were observed in 4 of 15 females in the 350 ppm group and 5 of 9 females in the 1200 ppm group. Based on these observations the NOEL for this study was determined to be 110 ppm. This threshold would be crossed at application rates above 1.0 lb ai/acre, particularly with short intervals between applications. The chronic effects to egghatch and viability were observed in bobwhite quail at 1200 ppm dietary levels. The 350 ppm NOEL threshold for other chronic effects would be crossed at single application rates of less than 2.0 lbs ai/A. As some of these effects are observed early in the study it might be surmised that the effects in the field could result from early initial or continuous pulse exposures to malathion as opposed to growth effects (weight reduction) which might require a longer exposure period.

Acute and chronic reproductive effects to mammals are not expected at the proposed tolerance rates. Sublethal effects to nervous system functions caused by acetocholinesterase blockage may lead indirectly to reduced survival. In studies where test rats were exposed to malathion, reduced

ability to navigate a maze was observed (Desi, 1976). This could be serious if a small mammal's ability to relocate its shelter left it exposed to predators or unable to return to its young.

#### Risk to Invertebrates

The modeling results and field monitored residues indicate that aquatic acute risk, restricted use, and endangered species levels of concern are exceeded by 8 to 160 times for certain freshwater and marine invertebrates groups at application rates of 0.175 lb ai/A, the lowest rate labeled for malathion. For the higher rates the acute risk LOC's are exceeded by over 200 times. The chronic level of concern(0.06 ppb) is far exceeded at all application rates for malathion. Monitored levels of malathion have frequently (though not always) been observed at concentrations which would far exceed the 0.5 ppb level of concern for acute toxicity to invertebrates. In Florida, monitored background levels in urban ponds sometimes exceeded this level of concern **before** aerial applications for medfly control were made. During 1994-95 Medfly spraying efforts in Ventura County, California samples were taken from streams in the spray area after rainfall events and subsequently used in toxicity studies with the freshwater cladoceran, Ceriodahpnia dubia and the estuarine mysid, *Neomysis mercedis* (Fujimura, 1995-see summary in appendices). Samples taken during a storm event proved 100% toxic to all exposed test organisms within 2 to 24 hours. These results indicate that concerns for invertebrate survival in exposed urban streams and estuaries are warranted. Monitoring programs related to bollweevil eradication efforts in southeastern states have also yielded residue levels which would be considered to offer acute risk to invertebrates. In general, levels monitored in agricultural settings appear to be lower than in urban settings and therefore exceedances may be less severe and less frequent under agricultural scenarios. However, predicted EEC's still indicate potential hazard to inverebrates from most crop uses from spraydrift (when applicable) or runoff.

### Risk for Fish

Risk quotients indicating levels of concern for acute risk to fishes, restricted use, and endangered species are exceeded for freshwater and estuarine fish at registered application rates of 0.5 lb ai/A, <0.175 lb ai/A, and <0.175 lb ai/A, respectively. Based on monitored residues, this will prove more likely if no protective restrictions are employed. The labels presently do not include actual protective methods (eg. buffer zones) for prevention of drift to aquatic habitats. Due to malathion's low persistence characteristics in water, chronic exposure risk for fish is less likely for single applications. Repeated applications could lead to continual exposure to peaks within one week periods, allowing for mean levels to remain above the chronic threshold of 2 ppb for early life stage effects. In actual uses of malathion (both urban and agricultural) many fish kills have been reported and confirmed. These incidents generally involve drift from aerial applications to small ponds, inland lakes, and rivers. In most cases the residues have not remained at high levels following these fish kills, indicating that fish are severely effected early in the exposure period. Fish kills resulting from runoff have also occurred several days after applications have been completed. These kills generally involve concentration of residues from a watershed into small feeder tributaries or stormwater feeder pipes which then open into retention ponds or farmponds within the drainage basin. Effects to estuarine fish have generally involved shallow lagoons or tidal waters at low tide following mosquito control uses.

## **Risk for Amphibians**

Routes of exposure for amphibians are expected to be through direct contribution of residues to aquatic habitats where adults or their offspring reside or through dermal adsorption from spraydrift to terrestrial areas where they might reside. Based on risk criteria for fish(½ the LC50 = Level of Concern) risk to tadpoles of sensitive frog species will occur with aquatic EEC's of 100 ppb. This

could occur from direct drift of less than 0.5 lbs ai/acre, or, using a high exposure GENEEC scenario, runoff and/or drift from an approximate 2.0 lb ai/acre application of malathion. EFED has limited information on possible effects to amphibians from dermal adsorption of residues. In actual reports of adverse effects to aquatic organisms mortality of adult amphibians (usually frogs) has been reported as well as presence of malathion residues in tissues following non-lethal exposures. These adverse effects generally involve malathion contamination of shallow wetland areas where flush rates are slow. Exposure of aquatic eggs or larvae of amphibians to malathion residues in surrounding water is also a potential route of exposure which could lead to adverse effects to developmental stages of amphibians.

## **Risk for Reptiles**

Acute risk for adult reptiles is not expected from most malathion uses. Oral ingestion or dermal adsorption of residue laden water might be the most likely route of exposure for aquatic reptiles. In several of the reported fish kills for malathion, adverse effects to aquatic turtles was also observed. However, confirmation that the turtles were killed by malathion alone is not provided. Effects to developing eggs of reptiles from direct exposure is also of concern when malathion uses provide potential exposure to shoreline nesting sites.

#### **Risk to Nontarget Plants**

Malathion is not expected to pose a serious hazard to terrestrial plants or aquatic algae as the mode of action (effects to nervous system) would not apply to plants. Malathion is expected to be systemically absorbed into plant tissues based on field study analyses of plant tissues after malathion applications. The Agency has received no reports of adverse reactions of crops or plants to malathion itself though label advisories for forest use do caution against application to certain species of trees.

### **Risk to Non-Target Insects**

Malathion has been shown to be lethal to many species of beneficial insects at rates routinely employed in agricultural settings. The routes of exposure may be direct contact, contact with foliar residues, and contact with residue coated pollen transported back to nests or hives. Aquatic larvae of terrestrial species may also be acutely effected for limited time periods through residue drift or runoff to streams or other aquatic habitats. In Giles' review of effects of malathion application to a hardwood forest (see previous summary) the author made a pertinent summary of the predictability of what may occur to insect populations. "Effects will range from none to near complete extermination of species on the area. Insecticidal effects on certain populations may be obscured by drastic predator-prey-host-parasite shifts caused by the insecticide. The resistance of natural populations and the immediate recharge and stabilization of populations will obscure effects of insecticides. Egg and larval stages, unmeasured by sampling techniques may be affected, the results of which may be postponed or may remain unrecognized. Aquatic populations may be affected with subsequent effects on insect eggs, larvae and later, adults. The result is a multidimensional web of action and interaction between and within species and their natural environment and an unnatural environmental hazard, malathion insecticide." This same summary may also be applicable to malathion effects when used near or over other non-agricultural areas containing beneficial insect populations, such as salt marshes, riverbanks, meadows and natural grasslands.

#### **Factors Influencing Malathion Exposure Levels**

The effect of lower application/use rates on aquatic malathion concentrations was examined using PRZM-EXAMS modeling. All input variables were those used in Mississippi cotton modeling except that the application rate was varied from 0.4 to 1.2 lbs / A (Table 41).

**Table 41**. Predicted aquatic malathion concentrations with varying application rates. Values represent the highest average concentrations expected in a ten year period. For example the highest 96-hour average concentration expected during a ten year period at 0.4 lbs/A is 23.551 ppb.

App rate							
(lbs/A)	YEAR	PEAK	96 HOUR	21 DAY	60 DAY	90 DAY	YEARLY
0.4	1/10	41.62	23.55	6.94	4.16	3.00	.93
0.6	1/10	61.96	35.06	10.34	6.20	4.47	1.39
0.8	1/10	83.22	47.09	13.89	8.33	6.01	1.87
1.0	1/10	103.44	58.62	17.30	10.37	7.48	3 2.33
1.2	1/10	123.75	70.12	20.68	12.40	8.95	2.78

PRZM-EXAMS modeling results suggest that peak and chronic aquatic concentrations directly correlate with application rate.

It is not possible to directly assess the effect of decreased application rate from monitoring data because application rates were constant at the locations of use. However, monitoring results suggest that the most important source of aquatic contamination is through spray drift. Table 10 shows malathion levels in undiluted runoff water. In 38 runoff measurements collected at distances of 0-135 feet from the treated field only once did the malathion concentration exceed 100 ppb and in most cases the concentration was less than 10 ppb. It is expected that runoff from fields would be diluted to varying degrees depending mostly on the size of the receiving water with larger bodies resulting in dilutions several orders of magnitude.

Because monitoring studies were conducted in a limited number of locations, all with soil types suitable for cotton, it is possible that soil half lives may be longer in other areas where malathion is used. Malathion persistence varies greatly in soil, ranging from less than one day to greater than five days. Soils with longer malathion persistence would be expected to have higher runoff potential.

Lower numbers of permitted seasonal uses at use rates in excess of 1.25 lbs ai/acre reduce length of exposure of sensitive bird species and possibly other equally sensitive terrestrial wildlife species to multiple peaks of malathion levels which are in exceedance of chronic concern levels. In addition the amount of residues potentially available for runoff would be reduced.

## **Multiple Application Intervals**

Terrestrial modeling results indicate that malathion degrades rapidly enough to avoid terrestrial residue buildup on vegetation in typical scenarios if intervals are 7 days or more. Slight increases in residues occur with 3 or 5 day intervals. Seven day or greater intervals appear to provide little residue increase over levels predicted for a single application.

#### Protective Buffer Zones

Monitoring studies have shown that buffer zones will reduce off-target spraydrift to aquatic habitats. This is particularly important when potentially exposed aquatic habitats are shallow or slowly flushed such as marshes.

#### Timing of Applications

In cases where beneficial pollinators are potentially exposed to toxic pesticides applications can be reduced during blooming periods or limited to dusk periods when pollinators are less active. Dawn applications may lead to more immediate exposure without the hours of potential degradation time offered by evening applications. However, it should be noted that this measure will not adequately protect beneficial insects from exposure to foliar residues. In the case of adulticide uses for control of saltmarsh mosquitoes, applications can be made during incoming tides to increase flush rate and provide additional dilution of residues that might drift to these habitats.

#### Storage conditions

Malathion degradation to products of higher toxicity under improper storage conditions is well documented, however effects due to impurities and degradates during normal use are not (with the exception of the mass poisoning of 2,800 spray men in Pakistan in 1976 resulting in 5 deaths, Aldridge *et al* 1979). Practices of major malathion using programs greatly reduce the amount of impurities and degradates released at application. Closely monitored programs using malathion (*ie* boll weevil and medfly eradication programs) are likely to have fresh stocks of pesticide and for the Boll Weevil Eradication Program the registrant removes remaining stocks at the end of pesticide spraying season. These factors reduce the probability of adverse effects due to degradates however it does not necessarily reflect normal operating conditions and procedures for smaller applicators which are not as closely monitored. Malathion stored for long periods of time clearly increases ecological and human health risks.

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# **APPENDICES**

# **APPENDIX 1**

# DATA REQUIREMENTS FOR Malathion

# Chemical No:057701

# 158.490 Wildlife and Aquatic Organisms

Guideline	Data In	MRID(s)	Data Req.
		Fulfi	illed
71-1(a) Acute Avian Oral, Quail/Duck	Yes	00160000	Yes
71-2(a) Acute Avian Diet, Quail	Yes	00022923	Yes
71-2(b) Acute Avian Diet, Duck	Yes	00022923	Yes
71-3 Wild Mammal Toxicity	No	Not Required	NA
71-4(a) Avian Reproduction Quail	Yes	43501501	Yes
71-4(b) Avian Reproduction Duck	Yes	42782101	Yes
71-5(a) Simulated Terrestrial Field Study	No	Not Required	NA
71-5(b) Actual Terrestrial Field Study	No	Not Required	NA
72-1(a) Acute Fish Toxicity Bluegill	Yes	40098001	Yes
72-1(b) Acute Fish Toxicity (TEP)	No	Required*(5,6)	No
72-1(c) Acute Fish Toxicity Rainbow Trout	Yes	40098001	Yes
72-1(d) Acute Fish Toxicity Rainbow Trout (TEP	) No	Required*(5,6)	No
72-2(a) Acute Aquatic Invertebrate	Yes	40098001	Yes
72-2(b) Acute Aquatic Invertebrate (TEP)	Yes	41029701	Partially**
72-3(a) Acute Est/Mar Toxicity Fish	Yes	41174301	Yes
72-3(b) Acute Est/Mar Toxicity Mollusk	Yes	40228401	No
72-3(c) Acute Est/Mar Toxicity Shrimp	Yes	41474501	Yes
72-3(d) Acute Est/Mar Toxicity Fish (TEP)	Yes	41252101	Partial **(5,6)
72-3(e) Acute Est/Mar Toxicity Mollusk (TEP)	Yes	42249901	Partial**(5,6)
72-3(f) Acute Est/Mar Toxicity Shrimp (TEP)	Yes	Required*(5,6)	No
72-4(a) Early Life Stage Fish(Freshwater)	Yes	41422401	Yes
72-4 Early Life StageEstuarine Fish	Yes	Required*(5,6)	No
72-4(b) Life Cycle Aquatic Invertebrate	Yes	41718401	Yes
72-5 Life Cycle Fish	Yes	Reserved	No
72-6 Aquatic Organism Accumulation	Yes		

Guideline	Data In	MRID(s)	Data Req.
			<b>Fulfilled</b>
72-7(1) Simulated Aquatic Field Study	No	Reserved	No
72-7(b) Actual Aquatic Field Study	No	Reserved	No
§158.540 PLANT PROTECTION			
122-1(a) Seed Germ., Seedling Enmergence	No	Not required	NA

122-2	Aquatic Plant Growth	No	Not required	NA
122-1(a)	Seed Germ./Seedling Emerg.	No	Not required	NA
122-1(b)	Vegetative Vigor	No	Not required	NA
123-1(a)	Seed Germ./Seedling Emerg.	No	Not required	NA
123-1(b)	Vegetative Vigor	No	Not required	NA
123-2	Aquatic Plant Growth	No	Not required	NA
124-1	Terrestrial Field Study	No	Not required	NA
124-2	Aquatic Field Study	No	Not required	NA
§158.49	90 NONTARGET INSECT TESTI	NG		
141-1	Honey Bee Acute Contact	Yes	05001991,001999,	
			05004151, 05004003	Yes
141-2	Honey Bee Residue on Foliage	Yes	4120800, 41284701	Yes
141-5	Fueld Test for Pollinators	No	Reserved	No
<b>§158.4</b> 9 141-1 141-2	90 NONTARGET INSECT TESTI Honey Bee Acute Contact Honey Bee Residue on Foliage	NG Yes Yes	05001991,001999, 05004151, 05004003 4120800, 41284701	Yes Yes

#### **FOOTNOTES:**

.

<sup>\*</sup>Required to support Malathion/Methoxychlor mixture products

<sup>\*\*</sup>Though formulation tests on 57EC were submitted the Agency requires formulation toxicity testing of Malathion/Methoxychlor mixture products

<sup>1. 1=</sup>Terrestrial Food; 2=Terrestrial Feed; 3=Terrestrial Non-Food; 4=Aquatic Food; 5=Aquatic Non-Food(Outdoor);6=Aquatic Non-Food (Industrial);7=Aquatic Non-Food (Residential);8=Greenhouse Food; 9=Greenhouse Non-Food;10= Forestry; 11=Residential Outdoor; 12=Indoor Food; 13=Indoor Non-Fod; 14=Indoor Medicinal;15=Indoor Residential

# **Environmental Fate Data Requirements**

<u></u>	Status	MRID Number
<b>Degradation</b>		
161-1 Hydrolysis	Fulfilled	
	(RJM, 12/15/92	40941201
	RJM, this review)	43166301
161-2 Photo water	Fulfilled	44.550.04
	(RJM, 12/15/92	41673001
161-3 Photo soil	RJM, this review) Fulfilled	43166301
101-3 Photo Son	(RJM, 12/15/92	40658009 41695501
	RJM, this review)	43166301
161-4 Photo air	Not required <sup>1</sup>	43100301
Tot i Thoto: un	(RJM, 12/15/92	40969301
	RJM, this review)	43166301
Metabolism	,	
162-1 Aerobic soil	Fulfilled	
	(RJM, 12/15/92	41721701
	RJM, this review)	43163301
162-2 Anaerobic soil	Not required	
102-2 Anacrobic son	Not required	
162-3 Anaerobic aquatic	Fulfilled	
•	(RJM, 12/15/92	42216301
	RJM, this review)	43163301
162 A Associa associa	Unfulfilled	
162-4 Aerobic aquatic	(RJM, 12/15/92)	42271601
	(RJM, this review)	43163301
<b>Mobility</b>	(RSIVI, tills review)	43103301
163-1 Leaching, Ads./	Fulfilled	
Desorption	(RJM, 12/15/92)	41345201
Description	(RJM, this review)	43163301
	( , , , , , , , , , , , , , , , , , , ,	43868601
163-2 Volatility-lab	Fulfilled	
	(RJM, 12/15/92)	42015201
163-3 Volatility-field	Not Required <sup>2</sup>	
<b>Dissipation</b>		
164-1 Soil	Fulfilled	
	(HLM, 7/25/91	41748901
	RJM, 12/15/92,	41727701
	this review)	43042401
		43042402
		43166301
164-2 Aquatic	Unfulfilled	
1	(RJM, 12/15/92)	42058401
		42058402
	(RJM, this review)	43166301

<sup>&</sup>lt;sup>6</sup>A study was submitted and reviewed but was not acceptable. Based on the laboratory volatility study, volatility does not appear to be an important route of dissipation; therefore, this study is not needed at this time.

164-3 Forest Not required	164-3 Forest		Not required
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<u>Status</u>	<u>MRID</u>
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164-5 Soil, long term Not required

Accumulation

165-2 Field rotat. crop Not required

165-3 Irrigated crop Fulfilled

(RJM, 12/15/92) 42058401 42058402

(RJM, this review) 43166301

165-4 Fish Fulfilled

(RJM, this review) 43106401

43106402 43340301

Spray Drift

201-1 Drop size spec. Not submitted<sup>3</sup>

202-1 Drift field eval. Not submitted

<sup>&</sup>lt;sup>3</sup> Data is not required at this time pending the results of the spray drift task force.

## **APPENDIX 2**

Tier I Estimated Concentrations for Surface-Water Exposure Assessment

#### Summary

Based on fate characteristics, model predictions and actual monitoring studies, the Agency predicts malathion will reach drinking water sources from the proposed uses. Surface water concentrations were modeled using the GENEEC model with acute and chronic drinking water levels set with the pesticide use scenarios that produced the highest aqueous pesticide levels. HED has indicated that malathion's degradate, malaoxon, is to be included in the tolerance expression for malathion thus water concentrations are provided in this document for both malathion and, when possible, malaoxon.

compound /		surface water	ground water		
exposure type	estimated concentration (ppb)	source of concentration	estimated concentration (ppb)	source of concentration	
malathion / acute	226	GENEEC peak	2.1	36 to 1 1	
malathion / chronic	21.2	GENEEC 56-day ave.	3.1	Monitoring data	
malaoxon / acute	96.0	GENEEC peak	2.1	Derived from malathion	
malaoxon / chronic	75.5	GENEEC 56-day ave.	3.1	monitoring data	

Table 1. Expected drinking water concentrations for malathion and malaoxon (Tier I).

EFED recommends that 226 and 96.0 ppb (Table 1) be considered as the highly conservative first tier estimates for acute surface drinking water levels for malathion and malaoxon, respectively. For chronic surface drinking water levels, 21.2 and 75.5 ppb are recommended for malathion and malaoxon, respectively. The chronic malaoxon value exceeds the chronic malathion level because of its longer expected environmental persistence. First tier groundwater concentrations were derived from monitoring data because they were higher than results from the SCIGROW model. The highest detected malathion concentration in groundwater accepted by EFED was 3.1 ppb. Malaoxon was not examined in this study but the same value is expected to be a conservative estimate of malaoxon concentration. EFED recommends exposure estimates of 3.1 ppb for malathion and 3.1 ppb for malaoxon in ground water.

This assessment was conducted under guidelines stated in OPP's Interim Approach for Addressing Drinking Water Exposure (November 1997), however, standard modeling techniques were modified to estimate malaoxon concentrations. Malaoxon levels were estimated with the GENEEC model with the <u>assumption</u> that fate variables which were not known are the same as those for malathion. Acceptable environmental fate studies specifically for malaoxon; including degradation, metabolism, mobility, dissipation, and solubility data; would be very useful for future assessments.

#### **Environmental Fate**

Based on all the data submitted, EFED concludes that the primary route of dissipation of malathion in surface soils appears to be aerobic soil metabolism. Supplemental data submitted by the registrant shows malathion degrades in soils with a half-life ( $_{T1/2}$ ) of <1 day on Blackoar loam soil

(pH 6.1). For modeling this half-life value was multiplied by a factor of three to estimate a 90th percentile  $t_{1/2}$  value, thus a 3-day half-life was used. This half-life is the same as the value used by USDA in malathion modeling (USDA 1991). EFED notes that longer half-lives (6.9 days) have been reported on sand (CalEPA 1996). Laboratory half-lives for anaerobic aquatic metabolism (<2.5 days) and hydrolysis (6.21 days at pH 7, 12 hours at pH9) indicate that these are also important routes of dissipation. Conversely, the compound is moderately stable to aqueous ( $t_{1/2}$  = 71 and 98 days) and soil photolysis ( $t_{1/2}$  = 173 days) and does not volatilize appreciably ( $\leq$  5.1% volatilized after 16 days).

Data presented to the Agency demonstrate that malathion is extremely mobile and thus runoff and leaching may be major routes of dissipation. Acceptable leaching data on parent malathion indicate that it is mobile in all soils tested [ $K_ds = 0.82-2.47$  L/kg,  $K_{oc}s = 151-308$  L/kg]. Terrestrial and aquatic field dissipation data indicate rapid dissipation ( $t_{1/2} = <2$  days). Malathion has been detected in ground water in three states at levels ranging from 0.007 to 6.17 ppb (USEPA 1992). Based on these data, EFED concludes that malathion has the potential to contaminate surface and ground water.

Malathion mono- and dicarboxylic acids, malaoxon, ethyl hydrogen fumarate, diethyl thiosuccinate, and CO<sub>2</sub> are degradates that have been found in malathion laboratory and field studies. Time course studies on malaoxon production on sand and soil have been published (CalEPA 1993) showing levels to increase over time. Maximal measured malaoxon concentration relative to initial malathion concentrations were 1.4% (after ~10 days on sand) and 10.7% (after 21 days on soil). Measurements past 21 days were not made. In the aerobic soil metabolism study submitted by the registrant 1.8% conversion to malaoxon was the maximum level observed on the Blackoar loam soil, thus 10.7% conversion appears to be a conservative conversion value.

EFED does not have a complete environmental fate database for malaoxon but based on its chemical similarity to malathion (sulfur is replaced by oxygen); the parent and its degradate are expected to have similar chemical properties. However, the biological properties of malaoxon are notably different in that it is more toxic than malathion. The aerobic half-life of malaoxon has been reported as 3 and 7 days in basic and acidic soils, respectively (Paschal and Neville 1976). This longer half-life is proposed to be a result of malaoxon's biocidal effect on soil microbes which contribute to malathion's degradation.

## **Surface Water Assessment**

GENEEC (USEPA 1995) is a screening model designed by the Environmental Fate and Effects Division (EFED) to estimate the concentrations found in surface water for use in ecological risk assessment. As such, it provides upper-bound values on the concentrations that might be found in ecologically sensitive environments because of the use of a pesticide. It was designed to be simple and require data which is typically available early in the pesticide registration process. GENEEC is a single event model (one runoff event), but can account for spray drift from multiple applications. GENEEC is hardwired to represent a 10-hectare field immediately adjacent to a 1-hectare pond that is 2 meters deep with no outlet. The pond receives a spray drift event from each application plus one runoff event. The runoff event moves a maximum of 10% of the applied pesticide into the pond. This amount can be reduced due to degradation on the field and the effects of soil binding in the field. Spray drift is equal to 1 and 5% of the applied rate for ground and aerial spray application, respectively.

Standard GENEEC modeling is inappropriate for malaoxon concentrations because the model assumes initial concentrations are highest which is not the case with malaoxon which increases over a period of weeks. In this case EFED chose a conservative scenario for modeling malaoxon concentrations by assuming that 10.7% of each malathion application is converted to malaoxon, thus for the purposes of GENEEC malaoxon was applied at 10.7% the rate of malathion. Data used for modeling were not ideal. The physical parameters used for malaoxon were those of malathion based on their chemical similarity. For the purpose of modeling EFED has attempted to estimate the upper 90<sup>th</sup> percentile of malaoxon's aerobic soil half-life value by multiplying 7 days (Paschal and Neville 1976) by a factor of three resulting in the model input value of 21 days. The aqueous half-life used was 107 days (based on malathion hydrolysis at pH 5), respectively. Both half-lives are expected to be conservative. The hydrolysis data for malathion is expected to be similar to malaoxon and is used in the absence of a half-life value in water with microbial activity.

Modeling results indicate that malathion and malaoxon have the potential to move into surface waters. Based on the inputs shown in Table 2 the peak GENEEC estimated environmental concentrations (EEC) of malathion and malaoxon in surface water is 226 and 96.0 ppb, respectively (Table 3). This estimate is based on the maximum application rate for citrus which represents the highest application rate for any crop used to support residue tolerances. EFED notes that higher use rates are reported on product labels but the registrant has stated they will not support rates greater than those defined in crop residue studies.

#### Acute exposure

EFED recommends that 226 and 96.0 ppb be adopted as a highly conservative estimates of *acute* first tier drinking-water exposure for malathion and malaoxon, respectively, based on the peak GENEEC value obtained with use on citrus and cotton.

#### Chronic exposure

EFED recommends that 21.2 and 75.5 ppb be adopted as highly conservative first tier estimates of *chronic* drinking-water exposure for malathion and malaoxon, respectively, based on 56-day average GENEEC concentrations obtained with use on citrus and cotton.

Table 2. GENEEC Environmental Fate Input Parameters (values are for malathion unless otherwise stated.)

DATA INPUT	INPUT VALUE	DATA ASSESSMENT	SOURCE
Application Rate	0.18-6.25 lbs ai/A	confirmed	Recommended usage rates
Maximum Number of Applications	1-25	confirmed	Recommended usage rates
Application Interval	3-30 days	confirmed	Recommended usage rates
Batch Equilibrium (Koc)	151 ml/g	Acceptable	MRID 41345201
Aerobic Soil Metabolism	malathion: $t_{1/2} = 3$ day malaoxon: $t_{1/2} = 3-7$ day (model input = 21 days)	Supplemental Supplemental	MRID 41721701 Paschal and Neville 1976
Solubility	145 ppm	Acceptable	Reported by registrant
Aerobic Aquatic Metabolism	t <sub>1/2</sub> = 3.3 day	Acceptable	MRID 42271601, 43163301
Hydrolysis (used for malaoxon aerobic aquatic t <sub>1/2</sub> )	t <sub>1/2</sub> = 104 day		MRID 40941201
Photolysis	$t_{1/2} = 94 \text{ days}$	Acceptable	MRID 41673001, 43166301

Table 3. GENEEC EECs ( $\mu g/L$ ) for certain malathion uses. The lowest and highest malathion userates and the use scenario for cotton were analyzed by GENEEC modeling.

		application		GENEEC EEC (μg/L)			
rate (lbs ai / A)	crop / interval (days)	11	-TT - 111-12-12		malathion		aoxon
( ,	( <b>,</b>	method	max # annually	peak	56-day ave	peak	56-day ave
0.18	Orange/7 grapefruit/7 lemon/7 lime/7 tangerine/7 tangelo/7 kumquat/7	aerial	10	8.24	0.78	3.10	2.44
0.50	Flax	ground	1	11.4	1.07	1.82	1.43
2.5	Cotton/3	ground	25	181	16.9	96.0	75.5
5.0	Pineapple/7	ground	3	224	20.9	47.3	37.2
5.0	Chestnut/7	ground	4	225	21.1	57.1	44.9
6.25	Orange/30 grapefruit/30 lemon/30 lime/30 tangerine/30 tangelo/30	ground	3	226	21.2	37.1	29.2

EFED notes that there is limited information available on the conversion of malathion to malaoxon during drinking water treatment. In a limited sampling of water entering and leaving a water treatment plant both malathion and malaoxon levels generally decreased after treatment, however, one sample showed an increase in malaoxon (USDA 1997). Data from sampling and analysis with a lower detection limit show a much higher rate of conversion (summarized further in the second tier assessment and Table \_)(personal communication, Dr. Marion Fuller, Florida Department of Agriculture and Consumer Services). EFED recognizes that conversion of malathion to malaoxon may be more efficient during water treatment than under conditions in the field, thus malaoxon may be present at a much higher concentration relative to malathion after water processing.

#### **Ground Water Assessment**

As EFED noted above, malathion has some mobility characteristics similar to other chemicals that have been detected in ground water. In addition, malathion has been detected in ground water in at levels ranging from 0.03 to 6.17 ppb in California (1 detection out of 499 wells sampled at a concentration of 0.32 ppb), Mississippi (2 detection out of 263 wells sampled at a range of concentrations of 0.03-0.053 ppb) and Virginia (9 detections out of 138 well sampled at a range of concentration of 0.007-6.17 ppb ); as reported in the EPA/OPP/EFED/EFGWB EPA Pesticides in Ground Water Data Base 1971-1991, National Summary. ERB1/EFED believes that malathion has the potential for movement into groundwater, especially on soils with low organic matter and high sand content.

Cheminova disputes the ground-water data reported in the PGWDB. In particular, it calls into question the analytical methods used to generate the data in the Virginia study. In addition, Cheminova indicates that the maximum detection in the study was 3.12 ppb, not 6.17 ppb. Noting Cheminova's doubts for the Virginia data, EFED suggests a ground-water concentration estimate of 3.1 ppb for malathion. This value is more conservative than SCI-GROW modeling results using use parameters for citrus or cotton as stated above. Since this monitoring result is specific for malathion EFED assumes the concentration of malaoxon will not exceed the concentration of malathion. Thus, EFED suggests conservative ground water concentration estimates of 3.1 ppb for malathion and 3.1 ppb for malaoxon.

#### **APPENDIX 3**

#### PRZM-EXAMS inputs

#### **Chemical-Specific Input**

Persistence and mobility numbers used in the first-tier GENEEC simulations were also used for the Tier II assessment. Chemical specific input parameters for PRZM and EXAMS are summarized in Tables X and .x. Certain assumptions were made for chemical dissipation parameters included in PRZM 3.1 but not GENEEC;

- 1. The aerobic soil-metabolism half-life of 3 days ( see following discussion) was used for the adsorbed and dissolved half-life throughout the soil column. Subsoil layers were assumed not to be anaerobic, as the deepest soil column simulated was only 150 cm deep;
- 2. A foliar decay rate of 0.126 d<sup>-1</sup> was used based on the 90% upper confidence limit of 37 foliar halflives reported in Willis and McDowell (1987).
- 3. Volatilization from the soil or foliage were not simulated (set to zero). Registrant submitted data suggest that volatilization is not an important route of dissipation;
- 4. Dissipation through plant uptake was not simulated;
- 5. Foliar wash-off of 0.5 cm<sup>-1</sup> was simulated, although data exists showing complete wash-off of organophosphate pesticides with the first 0.1 cm of rainfall.
- 6. An application efficiency of 95% was assumed for all application methods. As for GENEEC, drift from aerial applications was assumed to be 5% of the applied mass of malathion, and that from ground or airblast applications was assumed to be 1% of the applied mass.

The aerobic soil halflife for malathion chosen for modeling purposes was 3 days. This value is consistent with that used for USDA modeling in for malathion in the boll weevil eradication program which is the single greatest consumer of malathion. Degradation rates in soils vary greatly from the registrant supported halflife of 0.2 days to 11 days in rangeland soil with low organic content.<sup>4</sup> Open literature values are mostly greater than those observed in the acceptable submitted aerobic soil metabolism study. However, because the conditions and parameters controlled in the different open literature studies vary greatly it is not possible to calculate an upper 90th percentile limit of the values. In this instance, multiplying the registrant's submitted halflife value of 0.2 days by three to estimate the 90th percentile upper confidence limit did not produce a conservative value relative to published literature (Table 3). Using a single halflife value for modeling multiple scenarios is clearly a simplification in this instance but it is necessary to choose a value that is a conservative estimate of malathion degradation in agricultural settings used in modeling. The 3 day halflife chosen is not the highest available value published but conditions

<sup>&</sup>lt;sup>4</sup> Buckman, H.O. and Brady, N.C., 1969. The Nature and Properties of Soils. Macmillian Company, Collier-Macmillian Limited, London as referenced in USDA/APHIS National Boll Weevil Cooperative Control Program. Final Environmental Impact Statement Volume 1, 1991.

favoring very long persistence (*ie* very low moisture levels and microbial counts) are not expected to commonly occur in agricultural settings.

PRZM and EXAMS require that degradation half lives be converted into rate constants. The aerobic soil metabolism half-life of 3 days (as explained above) was converted to a daily rate constant for PRZM 3.1 by the equation Ln  $2/(T_{1/2})$ . The aerobic aquatic (input variable KBACW), anaerobic aquatic (KABCS), and photolysis (KDP) half-lives for EXAMS were converted to hourly rate constants using the formula Ln  $2/(T_{1/2} \times 24)$ . Hydrolysis half-lives at pH 7(KNH) and pH9 (KBH) were converted to rate constants by solving two simultaneous equations with the stable pH5 (KAH) constant set to zero.

Table 3. PRZM 3.1 input parameters for Malathion						
Input Parameter	Value	Quality of Data				
Foliar Volatilization (PLVKRT)	0 d <sup>-1</sup>	Poor				
Foliar Decay Rate (PLDKRT)	0.126 d <sup>-1</sup>	Supplemental				
Foliar Wash-off Extraction Coefficient (FEXTRC)	0.5 cm <sup>-1</sup>	Poor				
Plant Uptake Fraction (UPTKF)	0	Poor				
Partition Coefficient (Koc) for all crops	151 L kg <sup>-1</sup>	Acceptable				
Dissolved Phase Decay Rate: All Horizons (DWRATE)	0.231 d <sup>-1</sup>	Fair				
Adsorbed Phase Decay Rate: All Horizons (DSRATE)	0.231 d <sup>-1</sup>	Fair				
Vapor Phase Decay Rate (DGRATE) (all horizons)	0 d <sup>-1</sup>	Poor				

Table 4. EXAMS Input parameters for Malathion.					
Input Parameter	Value				
Aerobic Aqueous Metabolism Constant (KBACW)	8.82 x 10 <sup>-3</sup> h <sup>-1</sup>				
Sediment Metabolism Constant (KBACS)	3.78 x 10 <sup>-3</sup> h <sup>-1</sup>				
Acid Hydrolysis Rate Constant (KAH)	0 h <sup>-1</sup>				
Neutral Hydrolysis Rate Constant (KNH)	4.10 x 10 <sup>-3</sup> h <sup>-1</sup>				
Alkaline Hydrolysis Rate Constant (KBH)	$5.46 \times 10^3 \mathrm{h^{-1}}$				
Photolysis Rate Constant (KDP)	2.95 x 10 <sup>-4</sup> h <sup>-1</sup>				
Partition Coefficient (KOC) for all modeled crops	151				
Molecular Mass (MWT)	330 g ⋅mol <sup>-1</sup>				
Solubility (SOL)	145 ppm				
Henry's Law Constant (HENRY)	0				
Q10 For The water Column (QTBAW)	2				
Q10 For Sediment (QTBAS)	2				

## **Crop-Specific Inputs**

#### Cotton

This input file was adapted from EFED's standard PRZM scenario for cotton grown on the Loring silt loam in Mississippi, dated April 10, 1998. This soil is located in Major Land Use Area (MLRA) 134. However, weather data from Major Land Resource Area (MLRA) 131 is suggested for this standard scenario, as it represents a closer weather station (Jackson, MS). Inputted modeling parameters are as follows:

Crop	Planting Dates	Harvest Dates	Application Dates	Application Method	
Cotton	May 1	Sept. 22	June 1 - August 12	Aerial	

Local dates for planting and harvesting cotton, and likely dates of malathion application, were from USDA Boll Weevil Eradication reports. This PRZM simulation reflects the maximum label rate (2.5 lb ai/a), number of applications (25/year) and application interval (3 days) sought by the registrants for methyl parathion on cotton. USDA notes that these usage parameters are extreme and only 2 of 1000 fields treated in the Boll Weevil Eradication Program received 25 applications. Quantitative usage statistics show the average application rate of malathion on cotton is 0.3 lbs ai / A.

### Sorghum

This input file was adapted from EFED's standard PRZM scenario for sorghum in Kansas grown on a Loring silt loam soil. The weather recorded for MLRA 112 was used for meteorological input. Leroy Brooks of Kansas Agricultural Extension provided information that malathion would be most likely used early in the season to control aphids and greenbugs. Typical application months would be May through July. Inputted modeling parameters are as follows:

Crop	Planting Dates	Harvest Dates	Application Dates	Application Method	
Sorghum	May 21	October 1	June 1-15	aerial	

#### Apple

Malathion is used in orchards in the Northwest including apples, cherries, pears and walnuts. The largest use is on cherries and apples but results from these scenarios are expected to similar to each other and other orchard crops. Franz Needleholter of Oregon State Agricultural Extension provided typical malathion application dates for northern Oregon cherries. Applications may begin in the end of May and typically end the beginning of August. The most intense period of malathion usage is in June. Inputted modeling parameters are as follows:

Crop	Bloom	Harvest Dates	Application Dates	Application Method	
Apples	April 1	December 15	June 1-29	air blast	

#### Citrus

A standard Florida citrus scenario was chosen to model malathion on this crop. Although more malathion is used annually in California it is expected that the Florida scenario would result in higher estimated environmental concentration because of the weather, agricultural practices, and soils. Andy Rose of the University of Florida Agricultural Extension provided information that insecticides may be used throughout the year in citrus agricultural but use may be highest in the summer months. Modeling parameters were as follows:

Crop	Bloom	Harvest Dates	Application Dates	Application Method
Citrus	May 11	August 1	June 1 - July 31	air blast

#### Lettuce

More than 14 California vegetable crops receive malathion treatments. The California lettuce scenario adapted from a cole crop scenario is expected to have similar results to several other California crops. Dr. Bill Chaney in Salinas with Agricultural Extension provided very useful information on lettuce grown in central California. Lettuce may be planted anytime from January through August and harvested anytime from April through November. No lettuce is grown in December to break lettuce mosaic virus life cycle. Insecticides are applied generally starting April 1. Modeling parameters were as follows:

Crop	Planting Dates	Harvest Dates	Application Dates	Application Method	
Lettuce	February 10	May 12	April 1-26	aerial	

#### **APPENDIX 4**

#### **Other Aquatic Monitoring Studies**

Environmental Monitoring for Malathion Residues in Selected APHIS (PPQ) Control/Eradication Programs. USDA, 1990.

#### (A) Florida Medfly Program

<u>Methods:</u> Water analysis of residue levels in canals, lakes, swimming pools located with 1/4 miles of spray sites in Florida. Samples were taken 24 hours prior to and immediately after malathion sprays (15 minutes) - 1985 - 24 samples taken. 1987 - 42 water samples. 1990 - 62 water samples taken.

Results: 15 minutes post application

1985 - 6 of 24 samples showed Malathion residues 0.2 - 2 ppb 1987 - 9 of 42 samples - Residue levels - 0.23 - 1.55 ppb 1990 - 56 of 62 samples Residue levels - mean 0.8 ppb 0.23 - 51 ppb mean average fluctuation 6 - 18 ppb - mean 9.4 ppb

After 48 hours residues degraded rapidly - most below detectable limits.

## (B) Grasshopper Control Programs

These monitoring programs were conducted in 13 states from 1984 through 1989.

<u>Methods</u>: Malathion applied at 8 oz ULV/Acre; Purity was 91% ai. Samples obtained from flowing or impounded waters, natural or man made and standing water within 1/4 mile of spray zone or in the spray zone. Samples collected 24 hours prior to application and 15 minutes after application. Some sites - daily sample up to 72 hours post application. Level of detection = 0.1 ppb.

<u>Results:</u> Residue ranges were from 0.11 to 85.11 ppb - Highest residues in Utah and Wyoming. Two day samples had residues of 0.3 - 18 PPB.

© Bollweevil Control Program: Monitoring was conducted in Alabama, Arizona, California, Florida, Georgia, New Mexico, Mississippi, N. Carolina, So. Carolina and Texas during the 1985, 1988, 1989 and 1990 cotton growth seasons.

<u>Methods:</u> Application rate was 12 oz./Acre of 93-96% malathion using ULV. Interval was as little as one week for multiple applications. Soil, water and vegetation samples were collected. Water samples were take from area within 1/4 mile of application sites. These included recreational areas, houses, buildings, endangered species habitat, cotton fields (multi-applications) and pond sample following rainfall which occurred 3 days post-app. Where runoff occurred daily samples were collected for 3-5 days depending on how soon after application rainfall occurred.

Results: In Alabama 48 of 82 samples had Malathion residues over 0.1 ppb. These ranged from 0.102 to 24.74 ppb. Only 1 site was over 20 ppb (all samples). In Florida 15 samples were taken with 8 having residues ranging from 6 to 48.6 PPB (the high Malathion residues less than 6 PPB. In Georgia post application mean average residues after 12 applications were 12.9 PPB (15 minutes), 5.18 PPB (1-5 days) 1.78 PPB (6-10 days) and 1.86 (11-71 days.) Testing to determine whether distance or amount of rainfall was a more important factor indicated that distance from the water was more influential in effecting residue levels.

Pesticide Residues in Hale County, Texas, Before and After Ultra-Low Volume Aerial Application of Malathion. Guerrant, G.O. et al Pesticides Monitoring Journal, 1970.

Methods: Mosquito control June - August 1967 near Plainview and Abernathy Texas. Applied at 3.0 fluid oz/Acre by Air Force Tactical Air Command C 123 cargo planes based with 4500th Air Base Wing in Langley, AFB, Va. Altitude: 150 feet. Speed 150 mph. Winds <10 mph. Filter papers used to collect residues.

<u>Results:</u> Average concentration following 20 applications on June 16-22 was  $1.5 \text{ MG/FT}^2$  or 65% of application rate. Hydrolysis studies of water samples stored in various PH solutions up to 20 days after treatment showed residue stability at pH 2 and 72-62% recovery in pH 4-6. At pH 7 and 8, 16% and 11% recovery were observed. Residues in 32 sites (field water) showed malathion residues of 0.00 to 0.50 ppm 4 hours post application which decreased to < 0.006 within 24 hours post application.

# Residue Monitoring Report submitted to the Agency as 6a2 information under Barcode D207975.

<u>Methods:</u> Surface water residue monitoring data from waters adjacent to California rice fields included bensulfuron methyl, molinate, thiobencarb, carbofuran, methyl parathion, and malathion monitoring results.

Results: For malathion the maximum reported residues were 0.17 ppb.

Malathion: Special Projects Report No. 84-9SP. Cornacchia, John W., 1984. A report to the California State Water Resources Control Board, Toxic Substances Control Program. This report not only summarizes fate and toxicity characteristics for the Board, but also reports on findings of the 1981 monitoring program carried out during Medfly eradication efforts in Santa Clara, Santa Cruz, and San Mateo counties.

<u>Spray Methods:</u> Aerial spraying during spring, summer and fall months. 6 or more applications were made per site at a rate of 2.4 oz. Cythion/acre as a malathion laced bait. Helicopter and fixed wing aircraft were used.

Monitoring Program Methods: Monitoring stations were concentrated in aquatic areas based on the value of fisheries resources supported by the watershed. Creeks and rivers were sampled 24 hours prior to spraying to establish background levels of contaminants. Post application samples were taken within 72 hours of spraying in the area. These sample scenarios were taken every 1-2 weeks during the spraying program. Some sediment and biota samples were also taken for analysis

of malathion/malaoxon residues. Some of the creeks were sampled daily. Fish kills were monitored more closely and fish tissues were analyzed as well as the water from the location of the kill. Population estimates were also made before and after spraying in the San Lorenzo River drainage area. Additional monitoring of storm water drains and urban creeks was conducted immediately following rainfall events during the spraying program. The spray zones ranged in size from 43 to 1264 square miles.

#### Brief Summary of Results:

Santa Clara Valley: Air samples following the spraying did not exceed 1 ug/m³. Average coverage efficiency was approximately 76% with an estimated 24% loss attributed to off target spray drift. Monitoring was carried out up through the 6th application only. Dissipation from teflon coated collection surfaces indicated a half-life of 2.96 days for malathion residues. Peak summer water sample residue levels in two creeks ranged from 0 to 152 ppb. Based on sampling efforts aquatic half lives from local creeks were calculated to range from 1.71 to 6.97 days with less than 5% remaining after 1 week. One creek actually showed a slight increase in residue levels following applications 3, 4, and 5. During fall spraying efforts more frequent rainfall events led to levels as high as 800 ppb in Adobe Creek. This sample level coincided with a fish kill in the creek. In one instance a spraying effort was continued during a rain event and sampling showed residue levels as high as 1000 ppb, also leading to a fish kill. In general fall monitoring of residue levels averaging below 30 ppb within 48 hours after spraying. Levels were elevated when rain events occurred as late as 6 days after application. Storm drains acted as point source discharges for concentrated residues into tributaries.

The first fish kill primarily involved sticklebacks, a sensitive creek species. Residue levels at the time of the kill were 81 ppb. Body tissue concentrations of 3.8 to 1.6 mg/Kg were measured. One sediment sample contained 21 ug/L of malathion, but all others fell below 10 ug/L. In one instance residue levels reached 15 ppb in a lagoon and estuarine trough receiving water from spray area tributaries after a storm event and a fish kill involving striped bass and starry flounders was recorded.

Santa Cruz County: Spraying was carried out from August to mid November. Sampling along the San Lorenzo River and it's tributaries produced residue levels of <0.1 ppb to 41 ppb. Half-life estimates based on these sample periods ranged from 1.67-3.67 days. In general, levels dropped to below 1.0 ppb within a week after application. Rainfall events within 36-72 hours after spraying produced 11 to 19% increases in recorded malathion residues.

San Mateo County: During a storm event malathion residues reached 103 ppb in Pascadero Creek. steelhead trout and stickleback fish kills were reported following the event.

Malathion Residue Detections in Field Studies for Mosquito Control Uses

<b>Description/Location</b>	Application Data	<b>Detected Residue Range</b>		
NW Florida near Pensacola Beach, Tagatz, M.E. et al, 1974 Mosquito News test site was saltmarsh plot measuring 85 x 115 ft and control site was similar size. A 10' wide 4' deep canal bordered marsh.	Thermal Fog-95% Technical in fuel oil-applied at 17500 cu. Ft/minute-applied 3 times with two week intervals at low tide.	Marshwater 6 hrs post applic.=5.2 ppb 12 hrs post applic.=<0.1 ppb Canal Water 6 hrs post applic.=0.42 ppb 12 hrs post applic.=<0.1 ppb		
Same study as above but applied to different sites=8.5 acre marsh -25 liter tubs also distributed in marsh	ULV application- 3 applicationstruck mounted-330 foot swath at rate of 0.64 fl. oz./acre.	After 3rd application: Tubwater:1 hr.=0.32 -1.52 ppb 6 hr=>0.5 - 0.58 ppb Marshwater: <0.05 ppb(ND)		
Texas-near West Galveston. Conte F.S. and and J.C. Parker, 1975-applied to 3 bayous and saline lake in a saltmarsh. Depth was 61-91 cm.	Aerial application at 85.7 g/hectare-airspeed 145 km/hr at 9.2 meter altitude.	Post application residues  Test I Test II and III  9 hrs: 3.0 ppb 1 hr: 2.0 - 2.5 ppb  24 hrs: 1.5 ppb 3 hr.: 2.0 - 3.2 ppb  33 hrs: 1.0 ppb 8 hr.: 1.5 - 2.4 ppb  48 hrs: 0.8 ppb 24 hr: 1.2 - 2.2 ppb		
Texas-Galveston, Proctor, R.R. J.P. Corliss, and D.V. Lightner, NMFS, Gulf Coastal Fisheries Center	Aerial application at 77.8 ml of 95% malathion/acre. Tests were conducted twice at different times for same test site-two weeks apart.	Measured residues post application Test 1- High tide Test 2 Low Tide 0 hr= 8.9 ppb 65.3 ppb 6 hr=7.0 ppb 69.0 ppb 24 hr=3.1 ppb 1.08 ppb 48 hr=0.5 ppb 0.05 ppb		

During the 1981 aerial application program to control medfly outbreaks the California Dept. Fish and Game documented the environmental effects of malathion laced protein bait applications on 23 inland streams during the first 10 spray sequences of the program. Application rate was 196 g/ha. First application was July 14, 1981. One liter samples were collected in amber glass bottles at 0.3 m. depth, closed under water(to prevent air pockets), placed on ice, chilled to 4 deg. C, and transported to the Dept. Of Food and Agriculture's Meadowview laboratory in Sacramento for analysis of malathion residues. Samples were taken within 24 hours before application or within 12 hours after application.

"The aerial applications produced noticeable pulses of malathion concentrations in the streams. The peak malathion concentrations generally diminished to previous pre-spray concentrations before the next application."

"The highest malathion concentrations recorded in streams were those during or immediately following rainstorms. On October 7, 1981, 800 ug/L malathion was recorded at Station 4.1 during a major rainstorm. In Stevens Creek (Station 8.2), the effect of rain runoff on malathion concentrations was dramatic; previously recorded post-spray levels averaged 4.4 ug/liter but increased to 159 ug/liter on October 27, 1981 immediately after a rainstorm. High concentrations of malaoxon were also seen in these water samples. At station 4.5A, malaoxon concentrations exceeded the malathion concentrations."

San Francisco Monitoring Program-Stream Samples Mean Monitored Levels in PPB

Station # and Location	Dates Monitored	Pre Application Mean(range)	Post application Mean(range)
1.1 Permanente Creek	7/14-8/10	0.3(0.2-0.5)	8.3(0.7-19.0)
1.2 Stevens Creek(El Camino)	7/14-8/9	2.9(1.7-4.0)	40.9(0-82.6)
2.1 Saratoga Creek	7/16-8/9	0	0.2(0.2-0.2)
3.1 San Tomas Aquino Creek	7/15-8/27	2.2(0.9-5.1)	57.4(0.3-157.0)
4.1 Los Gatos Creek	7/16-8/5	0.5(0-1.3)	2.5(0.6-5.4
4.2 Ross Creek	7/16-8/5	2.2(0.1-4.3	27.1(6.2-50)
4.3 Coyote Creek(Oakland Rd)	7/16-8/26	0.8(0.2-2.1)	3.1(0.4-10)
5.1 Coyote Creek(Kelly Park)	7/15-8/6	0.4(0.2-0.6)	1.0(0.3-1.6)
7.1 Belmont Creek	8/11-9/16	0.4(0.2-0.6)	20.1(2.8-81.1)
8.1 Adobe Creek	7/15-8/6	1.5(0-4.3)	19.6(1.0-54.0)
8.2 Stevens Creek(S.Creek Blvd)	7/15-9/24	0.3(0-1.5)	4.1(1.2-8.8)
8.3 Los Trancos Creek	7/19-8/26	0.1(0-0.2)	2.5(0.7-5.3)
10.1 Llagas Creek	8/13-9/22	0.3(0-0.5)	1.3(0-3.8)
10.2 Uvas Creek	8/13-9/22	0.5(0-1.4)	1.1(0-2.6)
12.1 San Lorenzo River(Felton)	8/15-9/22	0.3(0-0.5)	6.2(0-15.9)
12.2 San Lorenzo R. (Brookdale)	8/15-9/21	0.2(0.1-0.3)	6.4(0.7-17.0)
12.3 Loch Lomond Reservoir	8/24-9/21	0.1(0-0.1)	4.2(0.1-12.5)
12.4 Bear Creek	8/15-9/22	0.3(0.2-0.4)	12.5(1.0-39.0)
12.5 Boulder Creek	8/15-9/21	0.1(0-0.3)	10.2(0.2-41.0)
12.6 San Lorenzo R.(Saratoga Rd)	8/15-9/21	0.1(0-1.4)	0.3(0-0.6)
13.1 Coyote Creek(Metcalf Rd)	8/12-9/24	0(0-0.3)	0.5(0.1-1.0)
15.1 Alameda Creek	8/27-9/25	0.1(0-0.3)	1.6(0.4-2.9)
16.1 Pajaro River(Hwy 101)	9/1-9/24	0.7(0.4-1.1)	5.6(0.3-11.5)

Malathion /Malaoxon Concentrations Up and Down Stream of 4 Drainage Culverts

Station #	October 27 Malathion/Malaoxon ug/L	November 12 Malathion/Malaoxon ug/L
1.3A Upstream At Drain Downstream	449.5 / 164.5 569 / 384 361.5 / 169	328.2 / 30.4 231.2 / 21.2 253.2 / 22.1

4.4 A Upstream At Drain Downstream	2.0 / 0.8 142 / 147 23.5 / 22	38.6 / 26 37.5 / 13.5 37.9 / 26.9
4.5 A Upstream At Drain Downstream	137 / 212.5 188.5 / 250 169.5 / 231	32.0 / 18.4 50.0 / 13.8 37.3 / 19.3
1.5 A Upstream At Drain Downstream	159.0/ 68.0 434.0 / 166.5 156.5 / 68.0	52.3 / 14.8 292 / 57.5 62.5 / 14.8

Six different locations(sampling stations) in the San Francisco Bay estuary were monitored during the 1981 medfly eradication program. The samples represented prespray levels, levels after spraying during the dry season(July 15-Sept. 24), and during the rainy season Oct. 14-Dec. 13). No detections were recorded prior to spraying. Rainy season detections ranged from mean averages of 1.0 to 7.0 ppb whereas dry season detections were much lower and sometimes considered non-detects(below 0.1 ppb f detection). The table below summarizes dry and rainy season detection ranges and means for the six sample stations.

San Francisco Bay Estuary- Malathion Monitoring Results Dry and Rainy Seasons 1981

Station #	<b>Monitoring Dates</b>	Mean Avg.	Range
SF.1 Coyote Creek RR Bridge	7/20 to 9/24(dry season)	0.1	0.0-0.25
	10/14 to 12/13(wet season)	1.7	0.0-5.3
SF. 2 Alviso Slough at South	7/20 to 9/24(dry season)	0.1	0.0-0.25
Bay	10/14 to 12/13(wet season)	1.4	0.0-3.3
SF. 3 Guadalupe Slough at South Bay	7/20 to 9/24(dry season)	0.1	0.0-0.40
	10/14 to 12/13(wet season)	1.7	0.0-3.5
SF. 4 Stevens Creek at South	7/20 to 8/7(dry season)	N.D.	N.D.
Bay	11/3 to 12/13(wet season)	1.0	0.0-2.0
SF. 5 Palo Alto Yacht Harbor at buoy	7/20 to 8/7(dry season)	N.D.	N.D.
	No samples (wet season)	No samples	No samples
SF.6 Coyote Creek at	7/20 to 8/7(dry season)	N.D.	N.D.
Calaveras Pt.	11/3 to 12/13	1.0	0.0-2.0
SF.7 Guadalupe Slough midway point	dry season-no samples 11/3 to 12/3	No samples 7.0	No samples 0.0 - 18.0
SF. 8 Alviso Slough midway point	dry season-no samples 11/3 to 12/13(wet season)	No samples 7.0	No samples 0.0-16.0

(Impact on Fish and Wildlife From Broad scale aerial Malathion Applications in San Francisco Bay Region, 1981, State of California Resources Agency, Dept. of Fish and Game, Environmental Services Branch, Administrative Report 82-2)

# Office of Water - Red Book 1976 Jeff, G. Malathion Sensitivity of Freshwater Fish (Salmonids (4), centrarchids (3)

Environmental Monitoring Results of the Mediterranean Fruit Fly Eradication Program, Ventura County, 1994-1995. A.Bradley, P.Woolford, R.Gallavan, P.Lee, J. Troiano. State of California Environmental Protection Agency, Dept. Of Pesticide Regulation. EH-97-05, December 1997.

Methods: Air, soil surface and water residues were collected for analysis of malathion and malaoxon deposition levels following aerial application of malathion ULV and Nu-Lure bait mixture at an application rate of 102 gms malathion+ 789 ml of Nu-Lure per hectare. A 41 square kilometer area was dosed 14 times at night by helicopters flying at 130 km/hr 100 meters above the ground and equipped with 6 Tee Jet flat fan nozzles resulting in minimum swath width of 61 meters. Intervals ranged from 14 to 21 days between applications. Ground deposition to soil was recorded on 1 foot square absorbent material at 34 sites which were collected 30 minutes after application. Air samples where taken at 5 sites prior to, during and after applications were made. Water samples were collected at Conejo Creek at one site before entry of stream into the treated area and at a location where the stream exited the treatment area. These samples were stabilized by reducing pH to 3 by addition of hydrochloric acid. In addition, stream samples were collected following 3 heavy rainfall events on Nov. 7, Jan. 20, and March 21. These rainfalls occurred 3 to 12 days after the last application. Due to high readings of malathion residues in runoff after the first two rainfalls several additional sites further downstream and in an estuary 15 km away from the application area were sampled after the third event. In addition bioassays were performed on cladoceran and mysid species using stream samples following the Jan. 20 and March 21 events. Reported Results: Deposition ranged from 80% (first 2 sprays) to 30% (third spray) of theoretically expected rate based on application rate computations. Ground deposition ranged from non-detectable to 0.07 mg/m2. The highest average air sample level recorded was 5.0 ppt (0.067 ug/m3) during the 24 hour period following a spray. Water samples collected at the inflow site for Callegus Creek before application averaged 0.09 ppb of malathion and 0.04 ppb of malaoxon. Following application the outflow sample site malathion residues averaged 44 ppb (range=39-50 ppb). During the rainfall events the highest recorded level of malathion was 787 ppb and the highest malaoxon level was 160 ppb (12 days post application). The estuarine collection site (Mugu Lagoon) was sampled when a rainfall occurred six days after an application. The resulting residue concentrations were negligible during the storm, but rose to 11.2 ppb of malathion and 2.62 ppb of malaoxon 4.5 hours later. Fifteen hours later malathion had decreased to 0.16 ppb and malaoxon was not detected. No fish kills were reported, despite the high residue levels. However, bioassays performed with stream samples and Ceriodaphnia dubia and with estuarine samples and *Neomysis mercedis* produced 100% mortality within 2 and 24 hours, respectively.

<sup>\*</sup> Mentions Estimated pH-6 half-life = 5 months. At pH-8 estimated half-life = 2 wks (Weiss and Gaksttatter, 1964)

<sup>\*</sup>In Miami River monitoring 10% of original residues remained in Little Miami River (pH 7.3 - 8.0) after 2 wks (Eichelberger and Lichtenberg, 1971).

# Appendix 5

# Table 5bMalathion Crop Use Terrestrial EEC Range Estimates in ppm-Grasses and Seeds Cheminova and IR4 Supported Maximum Tolerance Rates

	Folia	r Dissi	pation T	1/2=5.5	Days	Number of Applications							
	Rate lb ai/A	Int. Day	1 grass- seed	2	3	4	5	6	7	8	9	10	12-25
A	0.175	7D	42-1.2									72-4.5	
В	0.50	NA	120-3.5										
С	0.61	5D	146-4.3				300-19						
С	0.61	7D	146-4.3	189-9	232-14								
С	0.61	14D	146-4.3	171-11									
D	0.76	10D	182-5.3				254-16						
Е	0.94	3D	226-7										
E	0.94	6D	226-7					420-26					
E	0.94	7D	226-7		357-22				384-24				
F	1.0	7D	240-7					407-25					
G	1.25	3D	300-8.8	505-32				854-53					
G	1.25	5D	300-8.8				614-38						
G	1.25	7D	300-8.8		475-30	490-31	505-32	509-32	510-32	511-32	511-32	512-32	512-32
G	1.25	14D	300-8.8	351-22									
Н	1.50	7D	360-10		571-36			611-38					
I	1.56	7D	374-11	425-16			631-39						
J	1.88	5D	451-13					943-59					
J	1.88	7D	451-13		715-45	747-47		766-48					
J	1.88	14D	451-13	528-33									

K	2.03	6D	487-14					908-57			
K	2.03	7D	487-14		772-48	806-50					
L	2.5	3D	600-18		1292-56						1905- 119
L	2.5	5D	600-18		1121-68						
L	2.5	7D	600-18		951-59		1011-63				
M	3.43	5D	823-24								
N	3.75	7D	900-26			1490-61		1527-96			
N	3.75	14D	900-26								
0	4.7	30D	1128-33	1153-40							
P	5.0	7D	1200-35	1696-52	1902-69	1987-87					
Q	6.25	30D	1500-44		1535-46						

Scenario to Crop Relation for Table 5b

**0.175 lbai/A** A10=Orange, Grapefruit, Lemon, Lime, Tangerine, Tangelo, and Kumquat

**0.50 lb ai/A B1**=Flax

0.61 lb ai/A C5(5D)=Sweet Corn, C2(7D)=Hops, C3(7D)=Beans, Corn, Rice, Sorghum, Wheat, and Rye

C2(14D)=Alfalfa, Clover, Lespedeza, Lupine and Vetch

**0.76 lb ai/A D5**=Blueberry

0.94 lb ai/A E1(3D)=Grass for hay, E4(3D)=Mushroom, E6(6D)=Strawberry, E3(7D) =Peppermint and

spearmint, E7(7D)=Macadamia

**1.0 lb ai/A F6(7D)**=Melons, Watermelon, Pumpkin and Winter Squash

1.25 lb ai/A G1(3D)=Grass for hay, G2(3D)=Field corn, G2(7D) Brussel sprouts, cauliflower, collards, kale,

kohlrabi G6(3D)=Mustards, G25(3D)=Cotton, G5(5D)=Watercress, G3(7D)=Rice, Sorghum, Wheat, Rye, Barley, Oats and Corn, G4(7D)=Blueberry(ULV), G5(7D)=Turnip, Broccoli, Apple, Sweet Corn, Beet, Horseradish, Parsnip, Radish, Rutabaga, Salsify G6(7D)= Cabbage and

Cherry(ULV), G7(7D)=Carrot , G8(7D)=Mango and Passion fruit , G9(7D)=Asparagus G10(7D)=Pears and Quince , G12(7D)=Guava and Papaya, G2(14D)=Alfalfa, Clover, Lupine,

Vetch and Lespedeza

1.5 lbs ai/A H2(7D)=Celery, H6(7D)=Okra

1.56lbs ai/A I2(7D)=Potato, Sweet potato, I5(7D)=Onion, Garlic, Shallot, Leeks

**1.88 lb ai/A J6(5D)**=Lettuce, **J4(7D)**=Blackberry, Raspberry, Loganberry, Boysenberry, Dewberry, Currant,

Gooseberry, J3(7D)=Cucumber, Chayote, J6(7D)= Strawberry, J2(14D)=Grapes

2.03 lbs ai/A K6(6D)=Strawberry(50%WP), K3(7D)= Spinach, Dandelion, Endive, Parsley and Swiss Chard,

K4(7D)=Blackberry, Raspberry, Gooseberry, Loganberry, Dewberry, Currant and Boysenberry

2.50 lb ai/A L25(3D)=Cotton, L3(5D)=Figs, L3(7D)=Mustards, Walnuts, and Pecans, L5(7D)=Peas

3.43 lb ai/A M5(5D)=Tomato, Pepper, Eggplant

3.75 lb ai/A N4(7D)=Apricots, N6(7D)=Cherry, N4(14D)=Peach and Nectarine

**4.7 lb ai/A O2(30D)**=Avocado

**5.0 lb ai/A P3(7D)**=Pineapple, **P4(7D)**=Chestnuts

6.25 lb ai/A Q3(30D)=Oranges, Grapefruit, Lemon, Lime, Tangerine and Tangelo

No Use Rate Recommended As of December 1997: Broccoli Raab, Chinese cabbage, Cranberry, Dates (Gowan Co. only), and Hops(not clarified).

The estimates of residues in the above table are not highly conservative as calculated foliar dissipation half lives were as high as 10.9 days in the Willis and McDowell report. A slight increase in residues is predicted from multiple applications.

Johansen *et al* (1965) conducted a study entitled Bee Poisoning Hazard of Undiluted Malathion Applied to Alfalfa in Bloom. Foliar residues were measured during this study, which is also referenced in the hazard portion of this document under non-target insect toxicity field studies. As can be seen the malathion residues appeared relatively stable on surfaces of alfalfa foliage for the first 4 days. It appears that washoff may have led to significant reduction of residues on vegetative surfaces. Degradation appeared marginal before the rainfall events.

<b>Table 6.</b> Malathion Residues on Alfalfa from Johansen <i>et al</i> (1965)			
Days Post Application	Measured Residues Control Plots in PPM	Measured Residues Treated Plots in PPM	Precipitation in inches
0		28.8	0
1		18.9-21.1	0
2		23.8	0
3		27.6	0
4	<0.1	28.2	0.02
5		8.2	0.26
6		2.3	0.01
7		4.5	0
14	<0.1	0.4	0
21	<0.1	<0.1	0

## **Malathion EEC Crop Scenario Correlations**

0.175 lb ai/acre

A10=Orange, Grapefruit, Lemon, Lime, Tangerine, Tangelo, and Kumquat

**0.50 lb ai/A B1**=Flax

0.61 lb ai/A

C5(5D)=Sweet Corn C2(7D)=Hops C3(7D)=Beans, Corn, Rice, Sorghum, Wheat, and Rye

C2(14D)=Alfalfa, Clover, Lespedeza, Lupine and Vetch

**0.76 lb ai/A D5**=Blueberry

0.94 lb ai/A

E1(3D)=Grass for hay E4(3D)=Mushroom E6(6D)=Strawberry— E3(7D)=Peppermint and

spearmint **E7(7D)**=Macadamia

**1.0 lb ai/A F6(7D)**=Melons, Watermelon, Pumpkin and Winter Squash

1.25 lb ai/A

G1(3D)=Grass for hay G2(3D)=Field corn G2(7D) Brussel sprouts, cauliflower, collards, kale, kohlrabi

G6(3D)=Mustards G25(3D)=Cotton G5(5D)=Watercress G3(7D)=Rice, Sorghum, Wheat,

Rye, Barley, Oats and Corn G4(7D)=Blueberry( ULV)

G5(7D)=Turnip, Broccoli, Apple, Sweet Corn, Beet, Chayote, Horseradish, Parsnip, Radish, Rutabaga, Salsify,

G6(7D)= Cabbage and Cherry(ULV) G7(7D)=Carrot G8(7D)=Mango G12 Passion fruit

G9(7D)=Asparagus G10(7D)=Pears and Quince G12(7D)=Guava and Papaya G2(14D)=Alfalfa,

Clover, Lupine, Vetch and Lespedeza

1.50 lb ai/A

H2(7D)=Celery H6(7D)=Okra

1.56 lb ai/A

**I2(7D)**=Potato and Sweet potato **I5(7D)**=Onion, Garlic, Shallot, Leeks

1.88 lb ai/A

**J6(5D)**=Lettuce **J4(7D)**=Blackberry, Raspberry, Loganberry, Boysenberry, Dewberry, Currant, Gooseberry

J3(7D)=Cucumber J6(7D)= Strawberry J2(14D)=Grapes

2.03 lb ai/A

**K6(6D)**=Strawberry(50% WP) **K3(7D)**= Spinach, Dandelion, Endive, Parsley and Swiss Chard

K4(7D)=Blackberry, Raspberry, Gooseberry, Loganberry, Dewberry, Currant and Boysenberry

2.5 lb ai/A

L3(5D)=Cotton L3(5D)=Figs L3(7D)=Mustards, Walnuts, and Pecans L5(7D)=Peas

3.43 lb ai/A

M5(5D)=Tomato, Pepper, Eggplant

3.75 lb ai/A

N4(7D)=Apricots N6(7D)=Cherry N4(14D)=Peach and Nectarine

4.70 lb ai/A

O2(30D)=Avocado

5.0 lb ai/A

**P3(7D)**=Pineapple **P4(7D)**=Chestnuts

**6.25 lb ai/A** Q3(30D)=Oranges, Grapefruit, Lemon, Lime, Tangerine and Tangelo